WASTE CHARACTERISATION AND WATER-RELATED IMPACT PREDICTIONS FOR SOLID MINERAL WASTES: A NEW APPROACH

Report to the Water Research Commission

by

J L BROADHURST[1]; Y HANSEN[2,3] and J G PETRIE[1, 2]

on behalf of

[1]Department of Chemical Engineering, University of Cape Town, South Africa
[2]Department of Chemical Engineering, University of Sydney, Australia
[3]Centre for Environmental Strategy, University of Surrey, England

ISBN 978-1-77005-576-6
Report No 1550/1/07

July 2007

EXECUTIVE SUMMARY

Background and Motivation

The environmental impacts of primary metal production and coal-based power generation are significant, and these industry sectors are facing increasing pressure to improve environmental performance and contribute to development that is consistent with sustainability principles. A particular concern relates to the large tonnages of solid waste produced by the resource-based industries each year, most of which is consigned to land disposal. Whilst maintaining the geotechnical stability of mine related structures during their operational life is paramount, it is the continued generation of contaminated leachate from solid waste deposits that is in fact the most serious and pervasive environmental problem faced by the industry. Although less spectacular than catastrophic failure, contaminated leachate has been found to result in prolonged degradation and pollution of the surrounding environment over the long-term, with adverse consequences in terms of biodiversity conservation; quality and use of natural resources such as soil and water; as well as health and socio-economic impacts on local communities. Whilst the implementation of closure planning has been relatively successful in dealing with conventional rehabilitation and reclamation issues such as physical stability and revegetation, there is increasing concern that current regulatory and industry policies and practices will not be sufficient to prevent post-closure impacts nor guarantee a risk-free “walk-away“ situation.

In order to be managed effectively, the potential impacts and risks associated with solid mineral wastes first need to be quantitatively predicted. Without reliable measurement of potential impacts, particularly over the long-term, there can be no meaningful plan to mitigate adverse effects, leaving limited avenues for improvement of environmental performance. Furthermore, in a legislative framework leaning towards preventative rather than remedial approaches, it is equally important that the quantification of environmental impacts and liabilities be brought into the early design stages of the project life cycle, where the choice of appropriate technology can effect a reduction in both the amounts of waste generated and the environmental hazards associated with the wastes.

That said, solid mineral wastes remain poorly characterised, and the release and ultimate fate of contaminants following waste disposal are little understood. Furthermore, available impact assessment tools are generally deficient in their ability to capture the complexity of solid waste impacts, with current approaches being either too simplistic or too abstract. The need to improve the way in which solid mineral wastes are characterised is driven not only by the limitations in terms of current databases and methodologies for the generation of such. There is also a requirement for a more systematic and rigorous approach which will ensure that the necessary data and information is integrated into the decision stages of a project life cycle in a time and cost effective manner.

Project Objectives

The overarching objective of this project was to enhance capabilities for the reliable quantitative prediction of water-related impacts associated with solid wastes from the mineral-based resource industries, and to provide a means of effectively integrating such information into decision-making processes relating to water-resource management.

More specifically this project aimed to:

1. Develop a generic and integrated methodology for predicting water-borne environmental impacts associated with solid mineral wastes

2. Demonstrate the generic methodology by means of a suitable case study.

Summary of the Key Project Outcomes

The Generic Methodology for the Quantitative Assessment of Solid Mineral Waste Impacts

The generic methodology for the quantitative prediction of impacts from solid mineral wastes, as developed in this study, can be summarised in six systematic steps, namely: 1) problem formulation; 2) qualitative and 3) quantitative waste characterisation; 4) leachate generation and 5) dispersion predictive modelling; and 6) impact quantification.

Step 1 – Problem formulation

Problem formulation, which essentially entails the identification of assessment outcomes, requirements and constraints, is strongly coupled to data collection. A mineral waste inventory database has thus been developed to facilitate the collation of relevant data in a manner which supports and guides subsequent environmental assessment steps. This database includes generalised process flowsheets and spreadsheet templates for each mineral sub-sector in South Africa, and contains relevant information about the environmental impacts of solid wastes, and their current management practices. Despite gaps in this database due to the absence of public-domain data, it nevertheless provides an important starting point for both the motivation and development of a methodological approach for holistic assessment of waste character and environmental risks in a disposal scenario.

Step 2 – Qualitative waste characterisation

Qualitative waste characterisation is carried out in two consecutive stages. Firstly, solid waste characteristics are predicted from a consideration of ore type and composition (i.e. waste origins), combined with knowledge of the process route from ore to waste (i.e. waste source). The second stage entails the prediction of key characteristics relating to criteria of environmental significance i.e. hazard potential and mobility. The systematic rule-based approach to waste characterisation developed within this study reconciles available empirical data with a fundamental understanding of the mechanisms and parameters influencing element behaviour and deportment during ore formation, extraction and beneficiation, and ultimately waste disposal. A qualitative understanding of the solid waste characteristics serves as an initial screening assessment of environmental significance, and is an essential part of the proposed risk-based impact prediction methodology. Based on this understanding, it is possible to determine the likelihood and potential nature of adverse environmental effects arising from the management of a particular solid mineral wastestream, and in so doing justify the development of model structures to predict this impact. The information generated also serves to guide and inform subsequent empirical and predictive modelling studies in the step-wise predictive methodology, ultimately allowing for more effective and reliable environmental impact predictions and performance assessments.

Step 3 – Quantitative waste characterisation

The third step in the methodology is quantitative waste characterisation. Here, the overarching objective is to generate data that can reliably forecast the potential generation and release of contaminated leachate in a given waste disposal scenario. Conventional approaches rely on the application of empirical methodologies to derive data pertaining to the chemical compositions, physical properties and leach behaviour of solid wastes under laboratory-scale test conditions. Whilst this approach has some value, conventional laboratory-scale methods can only provide a partial picture of the time-dependant leachate generation potential, and fail over the long-term. Furthermore, their limitation means that more than one empirical test is likely to be required in order to generate the necessary data and information.

The analytical framework developed here for integrated and systematic waste characterisation and leachate generation predications is comprised of a number of systematic and iterative stages, with progressive incorporation of accuracy and detail. Early (level 1) studies correspond to the qualitative waste characterisation step described above, whilst later (levels 2-5) studies are based on empirical laboratory testwork and contextual (and quantitative) analysis of derived results This approach provides information and data necessary for both conceptual and numerical leachate generation model development, and helps validate the qualitative waste characterisation data and information (level 1) .

Step 4 – Leachate generation prediction

The fourth step involves rigorous leachate generation modelling, which takes into account both the hydrodynamic and chemical reaction processes to determine the time-dependent concentration profile of mobile constituents at the interface between the waste deposit and the surrounding environment. The complexity of the leachate generation models, and consequently the reliability and accuracy of the generated results, are largely dependent on how much is known regarding the mechanisms of leachate generation and how readily these mechanisms can be incorporated into a modelling structure. Simple mathematical models based on level 1-3 estimates of contaminant availability as a function of time can be used, in conjunction with knowledge of bulk liquid flows, to derive estimates of the time-related concentration profiles in full scale deposits. This is extended here through the use of a rigorous mechanistic model which takes into account both the chemical reaction and physical transport mechanisms under non-ideal flow conditions, to give detailed, time-dependent contaminant release profiles.

Step 5 – Fate and transport modelling

Here, the fate and transport of leached contaminants are modelled to obtain their spatial and temporal distribution in the subsurface environment. This can be achieved using existing groundwater modelling tools which, in contrast to those for predicting leachate generation, have been the subject of extensive development work in recent decades. Groundwater flow and mass transport models vary in complexity and completeness, depending on the purpose for which they were developed. In many decision situations faced by the mining and minerals industry, detailed site-specific data is often lacking. A simple groundwater flow and mass transport model is thus developed for cases where full physical and hydrogeological characterisation of the site is either not warranted or unavailable. This model approach can be tailored to reflect region-generic or site-specific conditions where these are known.

Step 6 – Impact quantification

The final step in the methodology is to calculate an appropriate indicator of the spatially-and temporally-distributed contaminated concentrations which can be used in decision situations spanning policy and regulation, design, and operational management situations The approach taken here makes use of water quality guidelines to develop risk profiles of the area or volume of land impacted by a waste deposit. The so-called “impacted land footprint indicator” provides a useful measure against which variables such as upstream mineral processing conditions (which, after all, define the amount and composition of generated waste), waste management practices, disposal site location and design, and even primary ores can be readily assessed. This indicator can also be used to assess resource-based impacts, such as degradation of soil and water quality, which are of particular relevance to water-scarce regions such as those found in South Africa. The advantage of using standards as a measure of risk is that they can be adapted to reflect site or region specific differences in ecological sensitivity or background levels.

The Copper Sulphide Tailings Case Study

Application of the proposed methodology for the prediction of solid mineral waste impacts is demonstrated for the case of porphyry-type copper sulphide tailings, which are representative of broad classes of minerals tailings. This case study is comprised of three overarching tasks, namely: 1) a review and analysis of the available data and information pertaining to the copper sulphide ore–to–tailings impoundment system; 2) qualitative and quantitative characterisation; 3) quantitative assessment of the environmental impacts.

Task 1 – Review and analysis of the copper sulphide ore–to–tailings impoundment system

The case study begins with the collation of available data pertaining to the generation, management and weathering behaviour of generic porphyry-type copper sulphide tailings i.e. following a system boundary which spans the range of ore deposit → tailings deposit → leachate emission. The outcomes of this assessment confirmed the findings of previous investigators, i.e. that currently available data is incomplete, inconsistent and very uneven. Serious deficiencies include the compositions of the waste output streams (waste rock and tailings), the characteristics of the copper ore deposits from which they are generated, and the time-related emissions arising from their disposal. Despite these limitations, it is still possible to establish a qualitative understanding of the system (particularly with respect to the key factors and variables influencing the performance of such); which enables current data gaps and deficiencies to be identified.

Task 2 – Qualitative and quantitative waste characterisation

Qualitative characterisation of generic porphyry-type copper sulphide tailings involves addressing the above-mentioned data gaps and deficiencies by:

1) generating a comprehensive list of element concentration ranges and forms in typical porphyry-type copper sulphide tailings on the basis of their origins (i.e. characteristics of typical porphyry-type copper sulphide ores), coupled with an understanding of the distribution behaviour of ore components during milling and flotation (i.e. the source of the waste); and

2) identifying key constituents of potential environmental significance on the basis of the hazardous properties and relative mobilities of the constituents in a typical disposal scenario.

Generic qualitative waste characterisation is followed by the generation of quantitative data for a specific porphyry-type copper sulphide tailings sample, focusing on those characteristics of potential environmental significance. The focus is on the quantification of the relevant physical properties; analytical techniques for quantification of total element concentrations; analytical techniques for the quantification of mineralogical compositions; sequential chemical extraction (SCE) tests to determine the partitioning or distribution of elements; and tests designed to determine the capacity of a waste to generate or neutralise acid. These combined tools provide information on strategic components and the key reaction mechanisms and parameters controlling their release in a disposal environment. The empirical waste characterisation protocol has also been used to assess the validity and/or limitations of the generic qualitative predictions, and to identify opportunities to optimise current methodologies and protocols for the effective and reliable empirical characterisation of porphyry-type copper, and other base metal, sulphide waste streams.

Task 3 – Quantitative impact assessment

The water-related impacts associated with this copper tailings sample are quantified by means of predictive modelling of the time-related generation and dispersion of contaminated leachate. This information, when coupled with risk-based water quality guidelines, provides an effective decision support indicator, called the “impacted land footprint”, which gives a dynamic measure of the extent to which land mass is contaminated by dispersed leachates from solid waste impoundments. The leachate generation model developed here provides a sophisticated and accurate description of pyrite oxidation in waste deposits. A comparison of saturated and unsaturated tailings deposits was conducted, and consideration was given to covered impoundments to investigate the effects of reduced hydraulic conductivity and oxygen diffusion. The results of this case study task indicate that the unsaturated and uncovered deposit result in the largest metals (as represented by iron) and salinity impacted land footprints, as a direct result of the higher leachate concentrations and larger deposit area.

Closing Statement of Significance

The case study has demonstrated the full capability of the approach to environmental impact prediction developed in this project. The "impacted land footprint" indicator is a predictive tool, and thus supports prospective decision making, across a variety of contexts – planning, design and operation. Its credibility lies in the fact that it is based on holistic consideration of the full material life cycle of minerals – from ore extraction through to refining. Its value is reinforced by the fact that it can be used in generic situations, or, with suitable data, made site-specific. It provides a much more meaningful indicator of land- and water-related impacts from solid waste management practices than does any other indicator currently employed in environmental assessment. The increased understanding afforded by this approach provides opportunities to influence and control behaviour, and eventually optimise waste management and minimise environmental impacts across the entire life cycle of minerals' operations.

The Way Forward

Whilst the potential overall value of the approach for the quantitative prediction of solid mineral waste impacts has been demonstrated via the case study, further expansion and optimisation will increase both the confidence in, and usefulness of, the methodologies and criteria developed within this project.
Specific recommendations include expansion and upgrading of the mineral waste inventory database; improved characterisation and classification of ore deposits; and optimisation of current sequential chemical extraction (SCE) test methods, particularly in terms of complementing and validation quantitative mineralogical analytical techniques.

In order to maximise the usefulness and acceptance of this approach within the mineral resource-based industry sectors, it is also recommended that the knowledge gained through this study be captured in the form of a dynamic "expert system" model, which guides the selection, design and application of empirical methodologies and predictive models; and links the impacted land footprint indicator to other decision-support tools protocols and information management tools.

Capacity Development and Technology Transfer within the Project

Capacity Building

This project has contributed directly to three post-graduate project dissertations and one final year student project within the Department of Chemical Engineering at the University of Cape Town, namely:

- Broadhurst, JL (2006) Generalised strategy for predicting environmental characteristics of solid mineral waste – A focus on copper. *PhD thesis, University of Cape Town, South Africa (under examination).*
- Maluleke, WJ (2006) An experimental investigation of leachate generation predictions of waste from copper sulphide ore processing. *MSc dissertation, University of Cape Town, South Africa (under examination)*

- Maidza, T (2006) Development of a rapid laboratory predictive test method using fluidised predictive techniques for the determination of oxidisability of residual Cr(III) present in slags. *MSc dissertation, University of Cape Town, South Africa (under examination)*
- Moholoopa, L and Lejakane, T (2006) Hydrometallurgical recovery of manganese from a manganese processing waste stream. *CHE4045Z chemical engineering project report, University of Cape Town, South Africa.*

The project has also supported and enhanced the capabilities of the Mineral Waste Classification and Characterisation Centre within the Department of Chemical Engineering at UCT. This centre has been specifically set up as a service facility to the local mineral industry, to enhance environmental performance and reduce environmental degradation and liability associated with its operations. Over the past 18 months, work on behalf of Namakwa Sands Smelters, Eskom, Enviroserve and the Skorpion Zinc operations in Namibia was undertaken.

On the basis of the expertise and knowledge gained from the project work, Dr H von Blottnitz, Dr Y Hansen and Ms JL Broadhurst have been involved in consultation on, and review of, the proposed Department of Water Affairs and Forestry Minimum Requirements technical background documents, namely:

- Risk Assessment Methodology for Metallurgical Waste Disposal by Landfilling
- Laboratory Leach Tests for Predicting the Impacts of Secondary and Waste Materials on Groundwater and Surface Water Quality.
- Criteria for Utilisation of Materials and By-product from the Metallurgical Industry.

A Background Briefing Paper for the National Sustainable Development Strategy on Solid Waste has also been compiled for The Department of Environmental Affairs and Tourism (DEAT) by Dr H von Blottnitz, with the assistance of Ms J L Broadhurst.

Technology Transfer

Technology transfer was conducted through the issue of written project reports and an electronic mineral waste inventory database, as well as through presentations at conferences. Conference presentations to date include:

- Broadhurst, JL; Petrie, JG and von Blottnitz, H (2004). *Understanding Element Distribution during Primary Metal Production: A Copper Case Study.* Paper presented at Minproc 2004 Conference, Cape Town, August 2004
- Maidza, T and von Blottnitz, H (2005) *Development of a Rapid Laboratory Predictive Test Method Using Fluidised Bed Techniques for the Determination of Oxidisability of Residual Cr (III) in Slag.* Paper presented at Minproc 2005, Cape Town, August 2005
- Broadhurst, JL; Petrie, JG and von Blottnitz, H. (2006) *Understanding Element Distribution during Primary Metal Production.* Paper presented at the Green Processing Conference, Newcastle, Australia, June 2006
- Maluleke, WJ and von Blottnitz, H (2006) *A Comparison of Two Sequential Extraction Procedures for Determination and Partitioning of Metals in Sulphidic Copper Tailings*. Paper presented at Minproc 2006, Cape Town, August 2006.

ACKNOWLEDGEMENTS

The research in this report emanated from a project funded by the Water Research Commission and entitled: *CLOSURE PLANNING IN THE MINERALS EXTRACTION INDUSTRY: THE ROLE OF EFFECTIVE WASTE CHARACTERISATION AND WATER-RELATED IMPACT PREDICTIONS FOR SOLID MINERAL WASTES.*

The steering Committee for this project consisted of the following persons:

Mr HM du Plessis	Water Research Commission (chairperson)
Mr DA Salmon	Anglo American Corporation
Mr L Labuschagne	Department of Minerals and Energy
Ms S Mudua	Department of Minerals and Energy

The financing of the project by the Water Research Commission and the contribution by members of the Steering Committee are gratefully acknowledged. In particular, the project team would like to thank Mr L Labuschagne of the DME and Dr H von Blottnitz of UCT for their advice, guidance and support.

The assistance of Margaret Ward and, posthumously, Sue Buerger for their administrative and professional assistance is also gratefully acknowledged.

TABLE OF CONTENTS

Chapter 3: Demonstration of the Methodology: A Focus on Porphyry-type Copper Sulphide Tailings 50

Appendices
(Note that the appendices are available only in electronic version on the accompanying CD)

Contents of accompanying CD

Electronic mineral waste inventory database:

- An electronic version of the flowsheets and spreadsheets generated for the local South African primary metal and coal-based power generation industries

Electronic report and Appendices:

- An electronic (PDF) version of this report and its Appendices

LIST OF FIGURES

LIST OF TABLES

Abbreviations

General text

ABA	Acid Base Accounting
ACMER	Australian Centre for Minerals Extension and Research
AD	Acid drainage
AMD	Acid mine drainage
ANC	Acid neutralisation (or neutralising) capacity
ANZECC	Australia and New Zealand Environment and Conservation Council
AP	Acid production (potential) - also referred to as MPA or APP
ARD	Acid rock drainage
BET	Brunauer-Emmet-Teller (surface area analysis)
DWAF	(South African) Department of Water Affairs and Forestry
EEA	European Environmental Agency
EC	Electrical conductivity
ERA	Environmental risk assessment
FAAS	Flame Atomic Adsorption Spectroscopy
GMI	Global Mining Initiative
HPLC	High performance liquid chromatography
ICMM	International Council on Mining and Metals
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
ILF	Impacted land footprint
LCI	Life Cycle Inventories
MMSD	Mining, Minerals and Sustainable Development (project)
NAG	Net Acid Generating
NAPP	Net Acid Producing Potential
n/d	not determined
NNP	Net Neutralisation Potential
NP	(acid) Neutralisation potential
NPR	Net Potential Ratio
PGM's	Platinum Group Metals
ROM	Run-of mine (ore)
SCE	Sequential chemical extraction (tests)
SETAC	Society of Environmental Toxicology and Chemistry
TDS	Total dissolved salts
UCT	University of Cape Town
US EPA	United States Environmental Protection Agency
US EPA CREAM	United States Environmental Protection Agency Centre for Exposure Assessment Modelling
WBCSD	World Business Council for Sustainable Development
WRC	Water Research Commission
XRD	X-ray diffraction

Units of measurement

^oC	degree Celsius (centigrade)-unit of temperature
cm	centimetre-unit of length (1cm = 10mm)
cm^3	Cubic centimetre-unit of volume

g	gram-unit of mass (1g = 1000mg = 10^{-3}Kg)
kg	kilogram-unit of mass (1kg = 1000g = 10^{-3}t)
kt	kiloton-unit of mass (1kt = 1000t)
m	metre-unit of length (1m = 100 cm = 1000 mm)
m^2	square metre- unit of area
mS/m	millisiemens per metre-unit of conductivity (1mS/m = 1000 S/m)
mg	milligrams-unit of mass (1mg = 10^{-3}g)
mV	millivolt-unit of electric potential (1mV = 10^{-3}V)
pH	measure of acid concentration (-log [H+])
ppb	parts per billion-unit of concentration (1ppm = 10^{-3}ppm)
ppm	parts per million-unit of concentration (1 ppm = 1 g/t = 1mg/kg in solids and 1 mg/l in solutions)
µm	micrometer-unit of length (1µm = 10^{-3}mm = 10^{-6}m)
s	second-unit of time
t	metric ton-unit of mass (1t = 1000kg)

Nomenclature

A_{max}	maximum area (units of L^2) or volume (units of L^3) of the impacted land footprint
$C_{m,x}$	concentration of substance *m* in stream *x*
$D_{m,x}$	unit mass of substance *m* in stream *x*
Eh	electrode potential relative to the standard hydrogen electrode
ΔG_f^o	Gibbs free energy of formation
K_f	equilibrium formation constant
L/S	liquid/solid (mass ratio)
$M_{t,\,x}$	total unit mass of stream *x*
σ^2	Impacted land footprint time variance with units of T^2
t_A	mean time for the temporal impacted land footprint (units of T)

CHAPTER 1: INTRODUCTION

The South African Minerals Industry is facing increasing pressure to improve its environmental performance. Environmental issues are now key determinants in decisions which affect the design of new technologies, as well as the operation of existing processes. The impacts associated with mining, minerals processing and coal-based power generation are significant. The management of large volumes of solid wastes and tailings pose a particular problem and overall environmental performance is largely a function of the success or failure of waste management strategies to minimise long-term liability.

In order for the industry to move towards sustainability, it must demonstrate that impacts are well managed and do not result in unacceptable or irreversible changes to the ecology (ICMM, 2002). This is difficult when wastes from these industries are typically poorly characterised and the mechanisms controlling leachate generation and subsequent contaminant migration not fully understood. While the adoption of sound waste management strategies has substantially improved environmental performance over the last twenty years, the management of impacts has relied heavily on monitoring – with action taken only once adverse impacts are evident or imminent. Without an adequate representation of solid waste impacts, the overall environmental performance of the industry cannot be assessed completely or accurately, leaving limited avenues for further improvement. There is thus a need for an approach that predicts the impact associated with environmental contamination arising from solid mineral wastes.

It is this need that this WRC-funded project attempts to address, through the development and demonstration of a risk-based methodology for the quantitative prediction of environmental impacts associated with solid mineral wastes – and the effective integration of such predictions into the decision-making processes relating to water-resource management.

Before developing such an approach, it is necessary to provide background information to set the problem in context. To this end, this chapter begins by highlighting the current situation and shortcomings thereof, and providing motivation for the need to address such shortcomings. This presents an opportunity to develop a conceptual approach from a scientific perspective which is applicable to typical solid wastes generated by the mineral-based resource industries. From this, the research hypothesis and associated objectives are developed. The chapter concludes with a brief description of the significance, scope and structure of the report.

1.1 Background and Motivation

The targeted metal in any ore deposit is present in relatively small quantities and the mineral-based resource industry sectors are thus characterised by large volumes of solid waste, with the share of ore that becomes waste typically varying from 25% in the case of the coal sector, to > 99% for the gold sector. A survey of Canadian metal mines (Warhurst, 2000) has indicated that, in general, the targeted metal or metal product accounts for only 2% of the mined ore – the remaining 98% being comprised mainly of waste rock (42%), mill tailings (52%), and slags (4%). Other solid wastes produced by the mining and minerals industry include flue dusts, residues from leaching and waste water treatment, and slimes and sludges from metal recovery operations.

Historically, the environmental legacy left by the primary metal production and coal-based power generation industries has not been a happy one, and these industries have thus become a target for environmental legislative bodies and lobbying organisations. Until the start of the 21st century, the industries response could be summarised by actions that have been aimed primarily at avoiding legal liability, international trade embargoes and consumer boycotts. The industry's position has changed considerably with the establishment of the Global Mining Initiative (GMI) under the auspices of the World Business Council for Sustainable Development (WBCSD) in 1998, and the completion of its research project entitled Mining, Minerals and Sustainable Development (MMSD) in May of 2002. Although the formal MMSD project initiative ended following the publication of the final report, international organisations such as the International Council on Metal and Mining (ICMM) have picked up on the industry's stated commitment to sustainable development, and have proposed consolidated courses of action. Whilst much of this relates to the Corporate Social Responsibility agenda, there is recognition too that a new research agenda is needed, and that, within this, a focus on better waste management and materials' stewardship is vitally important (Stewart et al., 2003).

This section highlights a number of relevant issues pertaining to solid mineral wastes from the mineral-based resource industries, with specific emphasis on the associated environmental impact and currently available tools for its prediction.

1.1.1 Solid mineral wastes and the environment

Solid wastes from the mining and minerals industry are traditionally disposed of to landfill, usually in the form of large heaps (dry waste) or slimes dams (wastes in slurry form). Despite their large volumes, historically such wastes were considered to be of low environmental risk, and until the middle of the 20th century were largely deposited in unengineered sites, frequently located in close proximity to the processing plants and/or local settlements. These disposal practises have led to a number of catastrophic failures, resulting in extensive environmental damage and, in some cases, even death (see discussions by Environment Australia, 1997; the MMSD project, 2002; van Zyl, 1993). Today strict legislative controls govern the site selection, design, management and rehabilitation of solid waste disposal sites, with significant technical advances having been made in the fields of geotechnical stability, and the control of dust and soil erosion.

Whilst maintaining the geotechnical stability of mine related structures during their operational life is paramount, it is not the only concern. Discussions in the open literature (see for example Dhar, 2000; Christie, 2002; Jarvis & Younger, 2000; Environment Australia, 1997; ICMM, 2002; MMSD project, 2002) indicate that it is the continued generation of contaminated leachate from solid waste deposits that is in fact the most serious and pervasive environmental problem related to the mining industry. As illustrated diagrammatically in Figure 1.1, leachate generation occurs as a result of water coming into contact with the solid waste. Whilst evaporation of this water may occur to a significant extent in dry climates, some liquid will also enter and percolate through the deposit, causing contaminants to leach into the liquid phase. As discussed in detail by previous authors (e.g. Hansen, 2004; Notten, 2001; Dallas & Day, 1993), contaminants associated with solid wastes from the primary mineral-based resource industries are typically salts and metals (including metalloids or semi-metals). Besides elevated metal concentrations and high salinity, leachates generated from solid mineral wastes also often exhibit extreme pH values. Highly acidic leachate is typically associated with solid wastes arising from the early beneficiation of sulphide ores, whilst a number of waste leachates, such as those arising from coal-combustion ash dumps and smelter slags, are very alkaline. Although less spectacular than catastrophic failure, subsequent migration of contaminated leachate within the surrounding environment can lead to ecotoxic and human toxic effects, and may also have an adverse affect on the quality, and consequently the usability, of water sources (ground and surface) and soils. Degradation of water sources is of particular relevance to water-scarce areas such as those occurring within South Africa, and recognition of this has prompted the South African Department of Water Affairs and Forestry (DWAF, 1998) to place considerable emphasis on the need for sustainable exploitation of water (in terms of quality, quantity as well as reliability of supply).

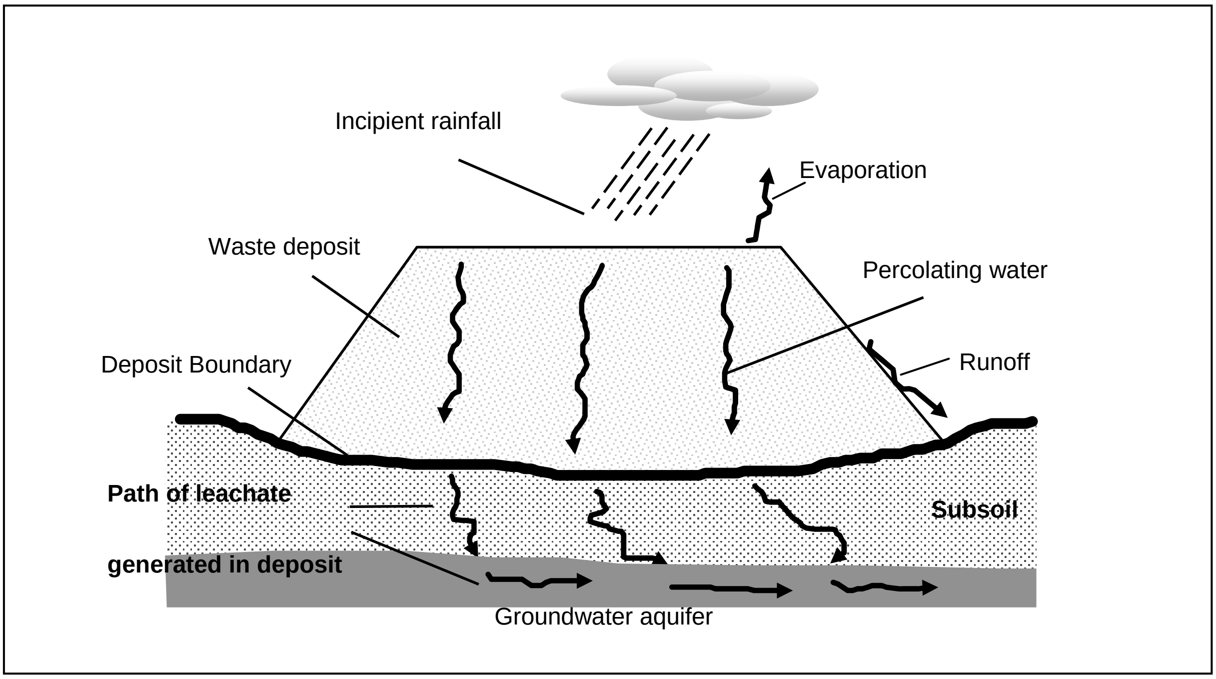


Figure 1.1: Leachate generation and transport from a solid waste disposal site (Hansen, 2004; Petersen, 1998)

Although the implementation of closure planning is reported by Danielson & Nixon (2000) to have been relatively successful in dealing with conventional rehabilitation and reclamation issues such as physical stability and revegetation, current regulatory and industrial policies and practices are still deficient in dealing effectively with chemical stability issues, and there is increasing concern that they will not be sufficient to prevent post-closure impacts and guarantee a “walk-away“ situation[1] (see further discussions by Barbour & Shaw, 2000; Christie, 2002; Grundy, 1997; Jarvis & Younger, 2000).

A recent workshop organised by the Australian Centre for Minerals Extension and Research (ACMER, 2006) highlighted some of the challenges facing the primary mineral-based resource industries in terms of successfully completing their mining operations, and emphasised the need for a more systematic assessment of the associated risks and liabilities.

1.1.2 Solid waste impact assessment: An overview of current tools and challenges

In accordance with globally accepted sustainability principles, all decisions relating to the development of primary resources are required to take into account the environmental (along with the economic, technical and socio-political) performance for all phases of the project life cycle – from exploration & feasibility through to post-closure. Recent years have seen the development of a number of analytical tools for assessing the environmental performance of processes and products, and ultimately for providing decision-makers with information on the environmental consequences of their decisions. These include Life Cycle Assessment (LCA), Environmental Impact Assessment (EIA), Risk Assessment (RA), Cumulative Effects Assessment (CEA) and Strategic Environmental Assessment (SEA), to name but a few. In the broader sense environmental assessment tools take the form of procedural frameworks of systematic steps for collecting, analysing, interpreting and communicating

---

[1] A walk-away situation is commonly referred to as one which delivers a maintenance free, self sustaining site which complies with acceptable environmental standards over the long-term without further interventions.

information pertaining to the environmental aspects of a product or process. Whilst the various environmental assessment tools can differ quite considerably in their purpose and methodologies, and even exhibit fundamental differences (see discussions by EEA, 1997 & 1998; Heijungs, 1995; Kirkpatrick & Lee, 1999; Partidario, 2000; SETAC, 1998; Stewart 2001; Tukker, 2000), a core element inherent to all environmental assessment tools is the prediction of the absolute or relative environmental impacts associated with the process or product.

Of particular relevance to the primary mineral-based resource industries is the ability to predict the potential water and soil-related local (and in some cases even regional) impacts associated with the land disposal of solid wastes. As pointed out by authors such as Warhurst & Noronha (2000), Mitchell (2000) and Jarvis & Younger (2000), without reliable estimations of these impacts there can naturally be no meaningful plan to mitigate the adverse effects. This pertains in particular to the post-closure environmental risks and liabilities outlined in the previous sub-section. Furthermore, in a legislative framework leaning towards preventative rather than remedial waste management approaches, it is equally important that the impact predictions are integrated into the early (strategic and tactical) decision-making stages, and are conducted in a manner that allows a clear link between the environmental impacts and the waste generation and management processes to be established. In this way, opportunities to reduce both the amounts of waste generated and the hazardous nature of unavoidable waste outputs at source (i.e. through the selection and application of appropriate ore processing routes and technology options) can be identified in the early scoping and design stages of a project. Discussions by a number of authors (e.g. Christie, 2002; Danielson & Nixon, 2000; Sassoon, 2000) have indicated that environmental impacts pertaining to mineral-based resource industries are frequently only addressed once all feasibility issues relating to the project have been resolved. This leaves little opportunity for improvement in environmental performance, particularly in terms of the post-closure impacts and liabilities associated with their operations.

Whilst forecasting potential environmental impacts, particularly in the early stages of a project, is arguably the most important element in an environmental performance assessment, it is also recognised as being the most challenging (EEA, 1998). This is particularly so in the case of solid wastes from the primary mineral-based resource industries, as the environmental impacts are not associated with the quantity of waste generated *per se* but rather with the generation of leachate, the subsequent migration of contaminants into the environment and their bioavailability. The mechanisms controlling these processes are complex and generally not fully understood. In addition, industry neglects to fully characterise solid waste streams, which is central to efforts to better understand leach behaviour. This is particularly the case in the early processing stages of commercial operations, with plant data and information focusing largely on technical criteria such as operational throughput and product quality. This trend is perpetuated by problems experienced in accurately sampling and assaying the large volume, low-grade process streams associated with the earlier beneficiation stages (particularly ore extraction, comminution and concentration), as well as uncertainty over what to measure. Even in cases where process streams are subjected to assaying, this tends to be based on broad assumptions and generalisations regarding minor elements and their dominant deportment routes, and the information mostly considered priority (Ayres et al., 2002). As a result, currently available data and information pertaining to the characteristics of waste outputs from mineral-based resource operations, and their subsequent behaviour under disposal conditions, is reported to be largely incomplete, inconsistent and very uneven (see for example discussions by Atkinson et al., 2006; Ayres et al., 2002; Hansen, 2004; Stewart, 2001). This is particularly so in the case of less commonly occurring or well-known minor and trace elements in waste outputs from ‘early’ beneficiation stages (e.g. waste rock and concentration tailings).

Difficulties also arise due to the fact that solid waste impacts are protracted and may persist for hundreds and even thousands of years. In addition, there is often a marked time lag between the generation of waste by the process and the appearance of adverse environmental effects. Leachate generation and mobility processes are also time-dependent and the resulting environmental concentrations are spatially distributed. The relationship between solid waste generation and resulting impact is therefore decidedly non-linear and a function of a multitude of process-specific, waste-specific and site-specific factors. Figure 1.2 attempts to summarise these factors and highlight the role of process, waste management and the environment on leachate generation and subsequent impact.

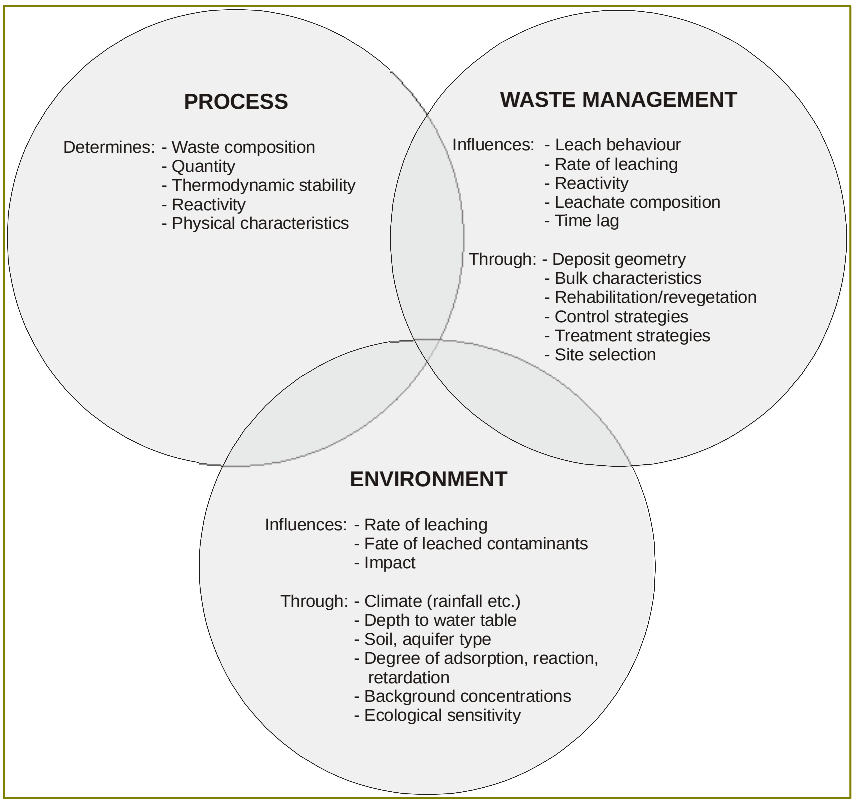


Figure 1.2: Spheres of influence on solid mineral waste impacts

The following sub-sections provide a brief overview of current approaches and methodologies for assessing solid waste characteristics and impacts.

Quantitative impact prediction modelling

The traditional approach to the prediction of contaminant release and potential environmental impact, which began evolving in the early 1980's, typically entailed designing laboratory-scale tests with the specific objective of simulating leachate generation or release under actual disposal conditions. Although this approach was based on the best understanding at the time, the continuing inability of laboratory tests to realistically simulate field conditions, and the inaccuracies associated with the extrapolation of short-term laboratory tests to full-scale waste deposits, has become increasingly recognised by industry and legislative bodies alike (see discussions by Eary et al., 1990; Environment Canada, 1990; Mattigod et al., 1990; Petersen et al., 2000; Stegemann & Cote, 1990; van der Sloot et al., 2003a; van der Sloot & Dijkstra, 2004). This recognition, coupled with the recent advancements in computational capabilities, has prompted the development of mathematical models to overcome limitations in empirical leach tests, and ultimately to aide in the prediction of leachate generation from solid waste deposits. Hansen (2004) conducted a comprehensive review and assessment of currently available environmental impact assessment tools as part of her doctoral thesis titled "Environmental Impact Assessment of Solid Waste Management in the Primary Industries-A New Approach", and found these to be “*generally deficient in their ability to capture the complexity of impacts associated with solid wastes from the primary resource-based industries*” as they were “*either too simplistic or too abstract*”. Simplistic approaches record the volume or mass of waste generated as an indicator of impact and thus ignore completely the interactions between the waste and the environment. Other more abstract approaches strive to define impact indicators that have some societal relevance and so tend to focus on the partitioning of contaminants in the environment and the resulting toxicological effects. By doing so, they pay inadequate attention to the fundamental processes that give rise to the elevated environmental concentrations in the first place. Current impact assessment tools also have difficulty incorporating the time-dependent and spatially distributed nature of solid waste impacts.

The complex compositions and chemical behaviour of solid wastes from the mineral-based resource industries adds considerably to the already significant challenges in reliably and accurately predicting the time-dependant release and spread of contaminants into the surrounding environment in a disposal scenario. Such wastes are generally comprised of a multitude of trace metals in various forms; the mobility’s of which are controlled by a complex network of competing parameters and mechanisms. As indicated by Mangold & Tsang (1991) and Hutson & Wagenet (1995), a predictive model which takes into account all the chemical reactions and hydrodynamic processes and parameters for all constituents would require more advanced computational facilities than currently exist, as well as extensive model input data. The major challenge to the reliable and intelligent application of impact prediction models to solid mineral wastes thus lies in the ability to minimise the complexities involved, through the application of meaningful assumptions and generalisations, without impacting on the accuracy of the results. In this regard, waste characterisation and data collection is an integral part of leachate generation modelling, particularly in terms of identifying key chemical and physical characteristics of the waste; the important reactions taking place; as well as the bulk transport behaviour. Furthermore, as postulated by Hansen (2004), the application of waste characterisation methodologies to identify one or two strategic metals, selected on the basis of potential environmental risk and for which the impacted land footprint can be assumed to encompass other metal footprints, will clearly reduce modelling efforts. This concept is discussed further in Chapter 2 of the report.

Solid waste characterisation for environmental impact predictions

In general, the characterisation of solid wastes can be based on a number of criteria including chemical compositions, physical properties, and leach behaviour. Of these characteristics, it is, however, the leach behaviour which is considered to provide the most pertinent information in terms of potential environmental availability and impacts of solid waste constituents, and which has been the focus of both industry and legislative bodies. As previously alluded to, the direct extrapolation of such empirical waste characterisation test results to full-scale waste deposits is fraught with inaccuracies and uncertainties. Nevertheless, in theory these tests can provide useful information on the behaviour of solid wastes, and may also be used to determine parameters needed in more detailed leachate generation modelling studies. In practice, however, the objective behind such procedures is frequently merely to classify or “type” wastes in accordance with local legislative requirements, rather than to provide a better understanding of the complex and time-dependant behaviour within the deposits, and/or to assess their dynamic potential to generate leachate (Petersen et al., 2000). As a consequence, empirical waste characterisation tests are frequently applied to wastes indiscriminately, and with little consideration to the material being tested and the key parameters involved. Prominent amongst these is the Toxicity Characteristic Leaching Procedure (TCLP) of the US EPA, which still enjoys widespread use around the world, despite its inadequacies and the uncertainties associated with its outcomes (Cohen et al., 1999; Hage & Mulder, 2004). This results in confusion and controversy regarding the interpretation and validity of the test results, and solid wastes that are poorly characterised.

In the specific case of solid wastes from the mineral-based resource industries, the development and application of suitable empirical characterisation protocols has been particularly limited, and has been identified by Hansen (2004) as one of the key requirement in terms of improving the reliability of effective solid waste impact predictions and management.

1.2 Improving the Way in which Solid Waste Impacts are Assessed: A New Approach

Discussions in the previous section have provided some insight into the environmental impacts and liabilities associated with solid wastes from the mineral-based resource industries, as well as the limitations and shortcomings associated with current tools for the meaningful and quantitative prediction of these impacts. This provides the opportunity and motivation for the development of a conceptual approach for solid mineral waste impact predictions which corresponds with the objectives of this study.

1.2.1 Statement of the problem

Accurate assessment of impacts is needed in order to make informed and appropriate decisions regarding the management and sustainability of mining and minerals processing activities. Without an understanding of leach behaviour and a method to quantify impact that takes into account the nature and behaviour of solid waste deposits, this cannot be achieved. Available impact assessment tools are deficient in their ability to capture the complexity of solid waste impacts, and the level of uncertainty and abstraction associated with their outcomes brings into question their applicability and relevance, especially to the generators of the wastes. In particular, no direction is given on ways to reduce impact as there is no sensitivity to process variables, waste management strategies or other site- and process-specific factors.

There is clearly scope to improve the way in which solid waste impacts are currently assessed. The motivation for improvement is, furthermore, based not only on a recognition of the limitations of current methods, but also on the need for a more rigorous approach for the mining and minerals industries in particular, where solid waste can often dominate the impact profile.

1.2.2 Research approach and objectives

The overarching objective of this research project is to enhance capabilities for the reliable quantitative prediction of water-related impacts associated with solid wastes from the mineral-based resource industries, and to provide a means of effectively integrating such information into decision-making processes relating to water-resource management.

In line with this objective, a new approach for solid mineral waste impact assessment is proposed, which attempts to address the challenges and current limitations outlined in the previous section. This approach, which has formed the basis of two recent PhD projects by Hansen (2004) and Broadhurst (2006), has as its first premise an extension of the conventional “cradle-to-gate” system boundary to include the ore and solid waste deposits as additional “unit operations” . As such, a clear link between the ores and processes from which the wastes originate, the management of the waste deposit and the resulting environmental impact is established (see Figure 1.3 for energy and metallic minerals). It furthermore places emissions from waste disposal on a par with other process emissions (such as direct gaseous and aqueous emissions) and effectively decouples leachate generation from its subsequent sub-surface transport. In this way the effect of feed ores, upstream operational and technology changes, as well as pollution control or waste management strategies can be evaluated, and this information used to improve environmental performance.

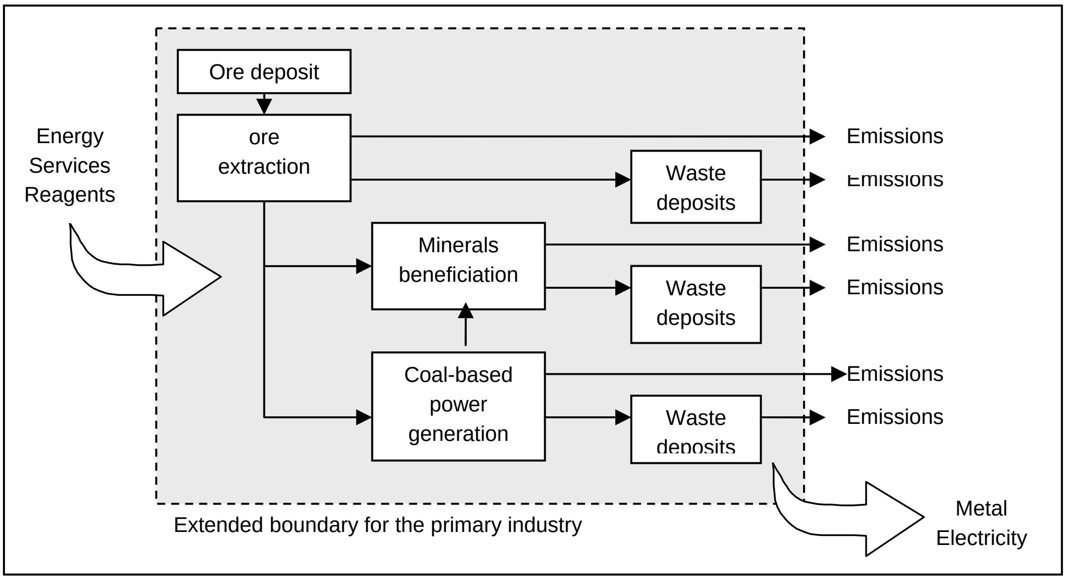


Figure 1.3: Extended process boundary for the primary industries

The second premise of this approach is that evaluation of the performance of solid waste management practices requires the inherent spatial and time-dependent nature of the resulting impacts to be quantified. Impacts arising from solid waste deposits are not instantaneous. As indicated in Figure 1.4, the release of contaminants into the environment is gradual and the generation rate and contaminant concentrations in leachate vary with time.

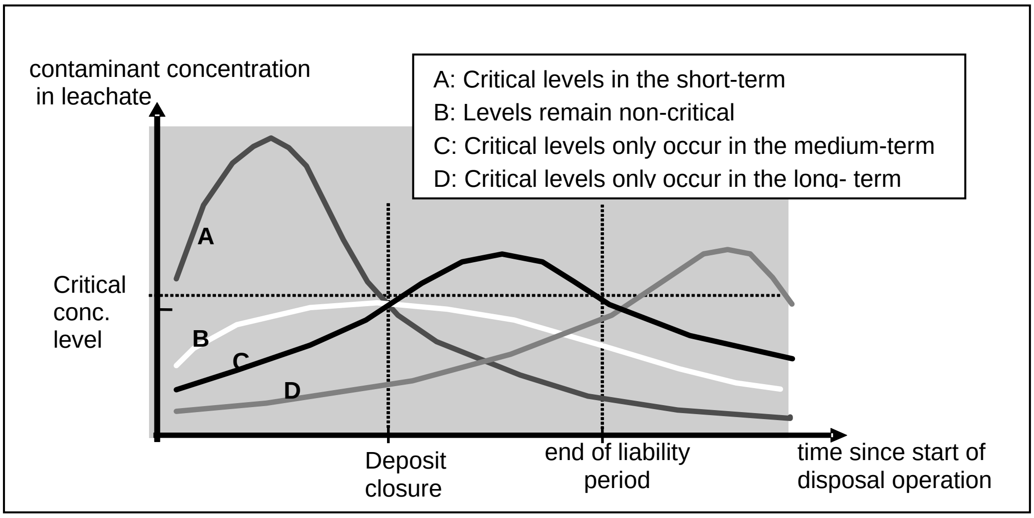


Figure 1.4: Potential contaminant concentration-time profiles in the leachate of waste deposits

Solid waste deposits are also point sources, meaning that resulting environmental contaminant concentrations are spatially distributed, typically decreasing with distance away from the source due to dispersion effects and geochemical reaction processes. Impacts from solid waste deposits are also felt on a local, or at most on a regional, scale (where a region is taken as a catchment area). Ignoring this behaviour by assuming homogeneous spatial distribution or approximating the magnitude and duration of leachate emissions has the potential to both underestimate and overestimate impact and miss impacts occurring at a local scale altogether.

The quantification of both the inherent spatial- and time-dependant nature of the environmental impacts is considered an essential feature of the proposed approach, and one which many of the current impact prediction tools fail to address adequately (see detailed discussions by Hansen, 2004). To achieve this, requires modelling not only of leachate generation processes, but also of the spread of the resulting pollution plume. Together, the leachate generation and contaminant dispersion models provide a measure of the rate and extent of the groundwater contaminant plume associated with a solid waste disposal site. In the proposed methodology, however, a distinction is made between leachate generation and contaminant dispersion, despite the fact that they have many processes in common and can be modelled similarly. This decoupling is significant and necessary for the effective integration of waste management into the process flowsheet. More specifically, the identification of opportunities to impact through engineering, managing and treating the waste dump, requires rigorous modelling of leachate generation as a function of upstream technological and process changes. Determining the fate and transport of contaminants on the other hand forms part of impact assessment, rather than waste minimisation opportunities. The tool selected for this purpose therefore needs to be more flexible to support different decision contexts and levels of data availability.

A third premise of the approach is that it is both necessary and possible to predict the key environmental characteristics of solid mineral wastes from a consideration of ore type and composition (i.e. the origins), combined with knowledge of the process route from ore to waste (i.e. the primary source). The structured prediction of key solid waste characteristics on the basis of origin and source essentially serves as a screening exercise, providing decision-makers with key information in the early stages of a project (in terms of developing processes within the context of sustainability), whilst simultaneously guiding further data collection and environmental impact prediction studies in the later project stages. A systematic and iterative procedural framework for the assessment of environmental impacts associated with solid mineral wastes, in which predictions of waste characteristics on the basis of their source and origin is a fundamental component, is outlined in Figure 1.5.

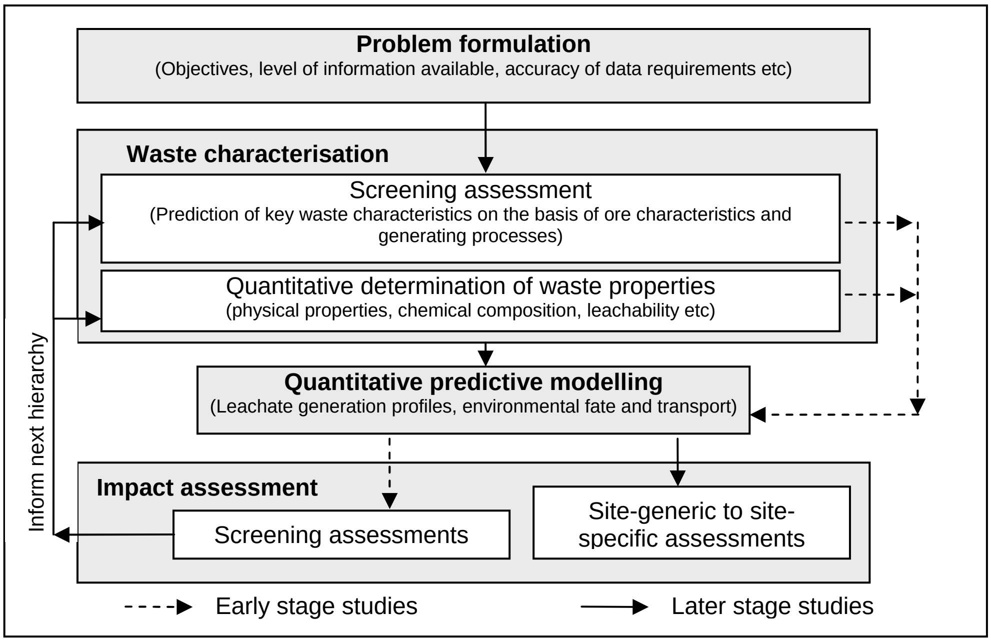


Figure 1.5: Procedural framework for the systematic assessment of environmental risks associated with solid mineral wastes

The proposed approach is compatible with risk-based environmental assessment methodologies, such as Environmental Risk Assessment (ERA), with modelling of leachate generation (emissions) and pollution plume spread (environmental concentrations) forming the necessary first steps in the assessment of environmental risks associated with a solid waste deposit. As indicated in Figure 1.6, the model outputs can, furthermore, be interpreted to provide a mid-point indicator of environmental impact based on easily measured effect criteria such as water quality, which can be biologically and deterministically linked to meaningful risk assessment endpoints (such as maintenance of biodiversity in a particular ecosystem). In this way the complexities, controversies and uncertainties associated with detailed exposure and effects modelling are avoided, whilst still attaining an indication of risk. The advantage of using standards as a measure of risk in the early decision stages of a project life cycle, is that they can be adapted to reflect site- or region- specific differences in ecological sensitivity or background levels in later, more detailed studies.

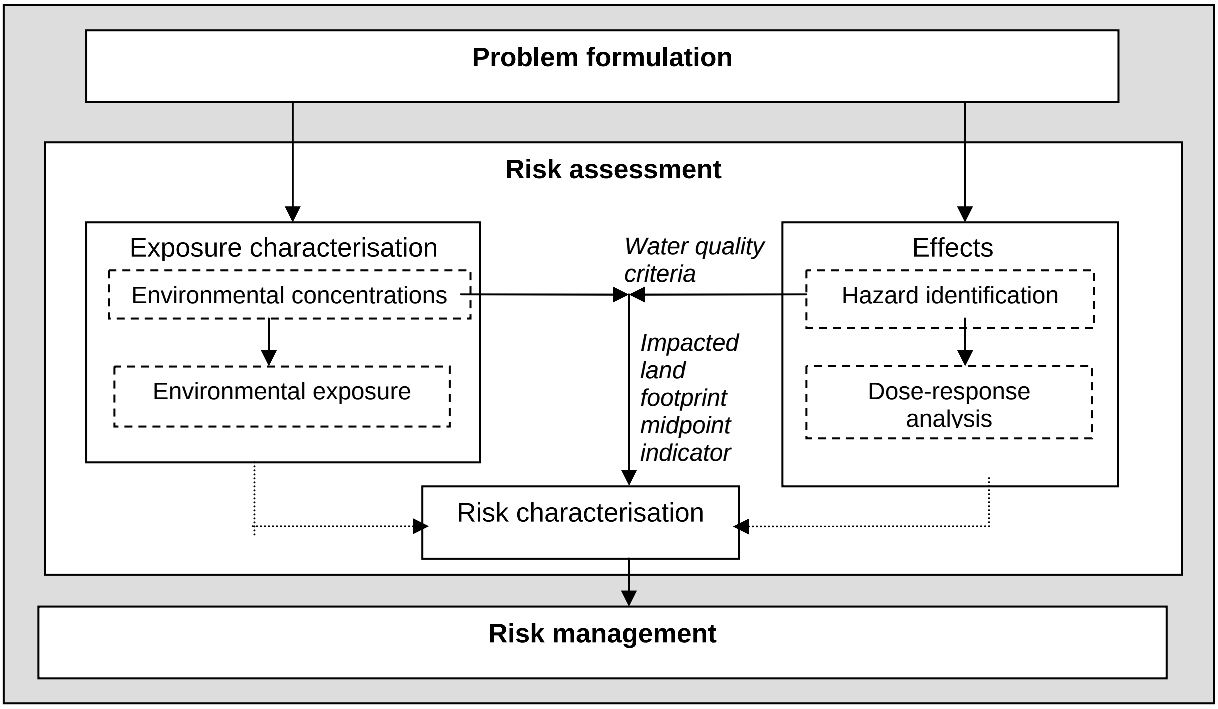


Figure 1.6: A risk-based environmental assessment procedural framework for solid mineral wastes

A comparison of spatially and temporally distributed environmental concentrations with water quality criteria provides an indication of the land area or volume impacted by the deposition of solid waste, as demonstrated in Figure 1.7. This quantitative indicator termed an “Impacted Land Footprint”, provides a useful measure against which variables such as upstream operating conditions (which, after all, define the amount and composition of generated waste), waste management practices, disposal site location and design, and even primary ores can be readily assessed. This indicator can also be used to assess mineral resource-based impacts, such as degradation of soil and water quality, which is of particular relevance to water-scarce regions such as those found in South Africa. It is the development of the necessary tools, models and assessment methodologies to enable the prediction of this ”impacted land footprint” which is the primary research output of this WRC-funded project.

In summary, the proposed approach is comprised of a number of systematic and integrated methodological components or steps, including:

Step 1 Problem formulation: Identify assessment outcomes, requirements and constraints

Step 2 Qualitative waste characterisation: Identify key environmental characteristics of solid waste outputs on the basis of origins (feed ores) and source (generating processes(es)).

Step 3 Quantitative waste characterisation: Quantify physio-chemical and leachate generation properties of the solid waste under typical or actual disposal condition.

Step 4 Leachate generation prediction: Quantify the time-related emissions to the environment arising from solid waste management.

Step 5 Fate and transport modelling: Determine the fate and transport of leached contaminants to obtain the spatial and temporal distribution of contaminants in the subsurface environment.

Step 6 Impact quantification: Develop a mid-point decision-support indicator based on these predicted environmental concentrations.

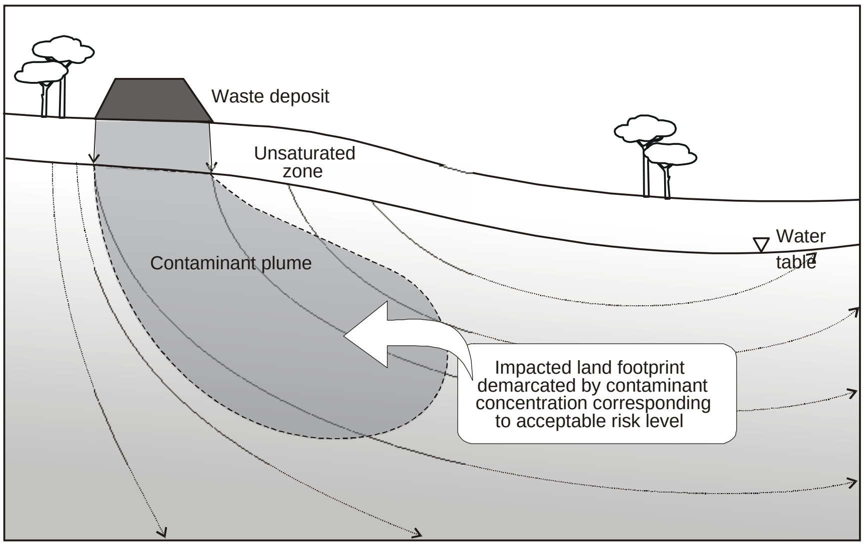


Figure 1.7: Impacted land footprint showing acceptable and unacceptable regions of contamination

The development of generic tools and protocols associated with each of these methodological steps (Chapter 2), and the subsequent application of the developed methodology to a tailings waste from the milling and flotation of a porphyry-type copper sulphide ore (Chapter 3), correspond with the two specific aims of this project. Finally, Chapter 4 discusses the significant findings and conclusions, and proposes a way forward. The report lay-out is represented schematically in Figure 1.8.

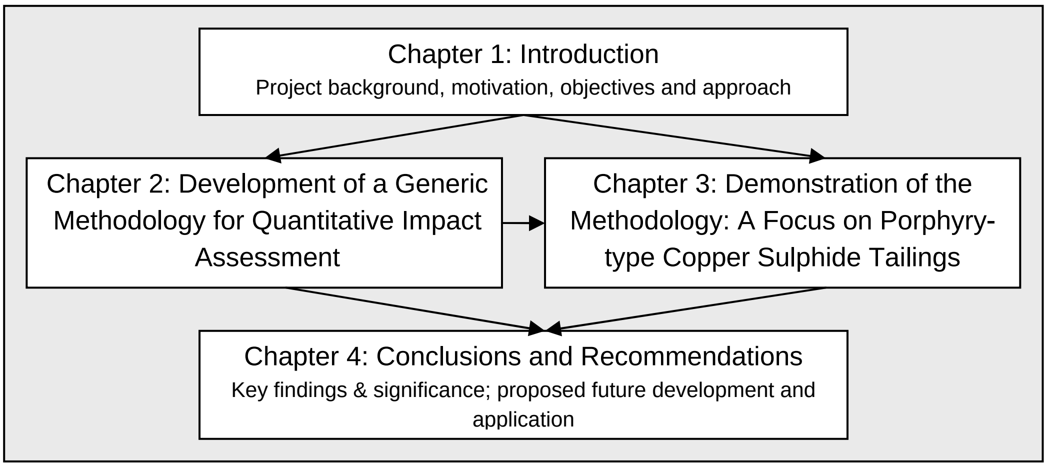


Figure 1.8: Schematic representation of the report structure

CHAPTER 2: DEVELOPMENT OF A GENERIC METHODOLOGY FOR QUANTITATIVE SOLID MINERAL WASTE IMPACT ASSESSMENT

As discussed in the previous chapter of the report, the proposed methodology for the quantitative assessment of water-related impacts associated with solid wastes from the production of metallic and fossil minerals can be summarised in six methodological steps, illustrated diagrammatically in Figure 2.1.

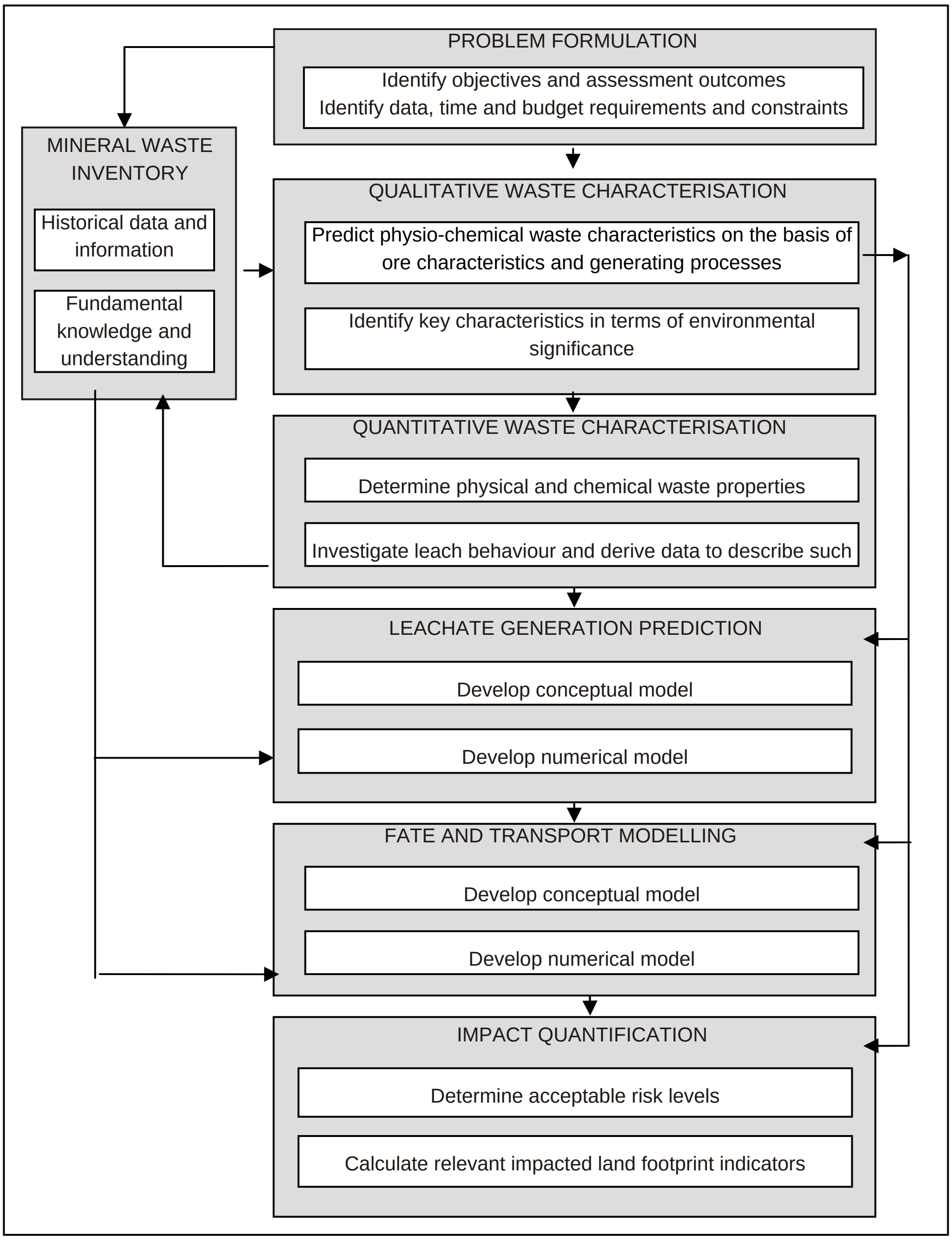


Figure 2.1: Conceptual methodological approach for the quantitative prediction of impacts arising from solid mineral wastes

This chapter of the report is aimed at developing the understanding, protocols and techniques which underpin the proposed approach, with each with each methodological step corresponding to a sub-section of the chapter.

2.1 Problem Formulation: Step 1

Problem formulation is the first step in the proposed methodology and perhaps also the most important, as decisions made here have a bearing on all other steps in the assessment methodology. Problem formulation essentially entails the identification of assessment outcomes, requirements and constraints. In order to be effective, problem formulation requires a comprehensive understanding of the system being assessed and, as such, is also strongly coupled to the collation of available data and information.

As already alluded to in the previous chapter, the lack of available data, as well as the poor quality of that which is available, has been generally identified as a major barrier to the effective analysis of primary mineral-based resource operations (see for example Atkinson et al., 2006; Ayres et al., 2002; Hansen, 2004; Stewart, 2001). In this regard, the scope of work pertaining to this step of the proposed methodology has been concerned largely with enhancing capabilities pertaining to the identification and collation of data and information, which is considered to be of key relevance in terms of quantitatively predicting and assessing the environmental impacts associated with solid mineral wastes. More specifically, this sub-section of the report aims to 1) develop a structured approach for the collation of appropriate data and information pertaining to primary mineral-based resource systems (Section 2.2.1); and 2) apply such an approach to establish a solid mineral waste inventory database for the South African metal and coal-based power generation industries (Section 2.2.2).

2.1.1 Identification and collation of relevant data and information: a structured approach

In the broader sense, the analysis of a mineral-based resource processing operation, in terms of informing subsequent performance analysis and decision-making, should serve to:

- define the system boundaries, as well as the unit processes and key parameters involved;
- characterise the relationship between process inputs and outputs;
- make existing information more accessible and comparable;
- identify current data gaps and deficiencies in terms of both availability and quality

In the first instance the system needs to be ““mapped” by means of a process flowsheet which identifies all relevant processes and arranges them in relation to one another. This flowsheet serves as a practical aide to the subsequent collection of all available and relevant data and information pertaining to the identified processes.

<u>Flowsheet construction</u>

The starting point for the construction of a flowsheet is to establish the system boundary encompassing all material flows and main processes of relevance to the specific operation under investigation. As discussed in the previous chapter, a key feature of the proposed approach is the extension of the conventional “cradle-to-gate” system boundary for describing mineral resource-based process operations to include the formation of ore deposits and the generation of contaminated leachate from solid waste deposits as processing stages of key significance in terms of overall environmental performance. The extension of the system boundary to include both the processing plant (in the case of ore extraction, ore beneficiation and waste management) and geochemical (in the case of ore formation and leachate generation) unit processes or operations is illustrated by the hypothetical process flowsheet in Figure 2.2.

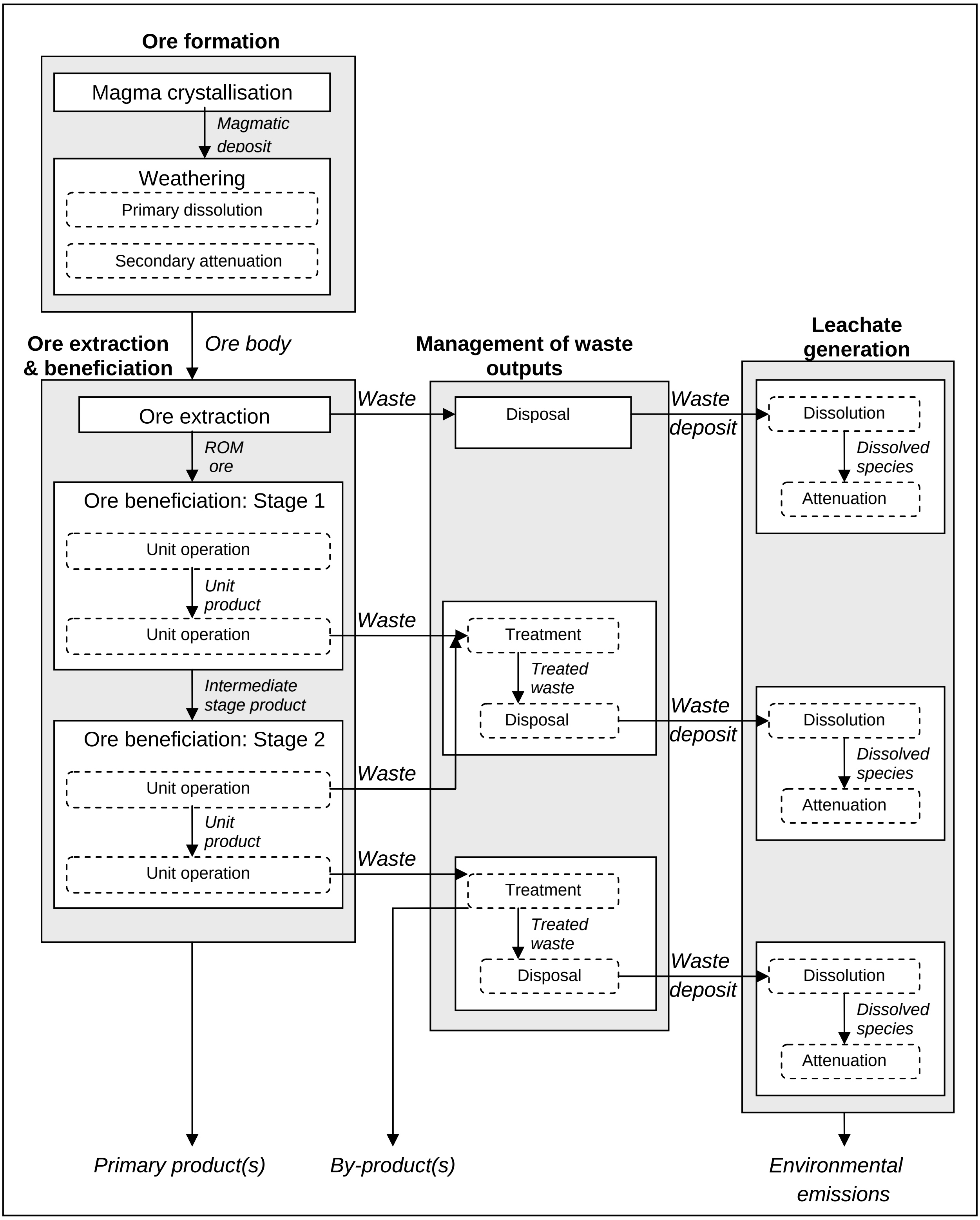


Figure 2.2: Hypothetical flowsheet for a mineral resource-based process operation

As pointed out by a number of other investigators (including Basson & Petrie, 2001; Notten, 2001; Stewart & Petrie, 2006), it is important that the flowsheets representing such complex systems are structured in a manner which not only facilitates predictions of relevant inventory flows, but which also limits information requirements and streamlines the collection thereof, i.e. the flowsheet should be as simple as possible but as complex as necessary. To this end, Stewart & Petrie (2006) have developed a set of heuristics to guide the selection and aggregation of unit processes in the construction of flowsheets for various mineral industry sectors (i.e. consistent with system analysis on an industry, national and/or global level). These are based on criteria relating to common function, mass flow rate, hazardous nature of the waste, common waste generation and energy intensity, as described in Table 2.1.

Table 2.1: Criteria for definition of unit process boundaries within generalised flowsheets (after Stewart and Petrie, 2006)

Criteria	Details
Common Function	If the function of process units is the same within different flowsheets, they are integrated into a single unit; for example since the crushing process on a gold plant is the same no matter what process route is followed thereafter, crushing is defined as a unit – comminution
Mass Flow Rate	Units which have a high through-put, high reagent addition or high waste generation will have an obvious effect on the LCI inventory model. They must be kept separate in order that their effect on the total waste stream is not obscured. This is the reasoning behind keeping the two different elution routes separate in the gold flowsheet.
Hazardous Waste	If a unit gives rise to a hazardous or toxic emission or requires a hazardous or toxic reagent in its operation, it must be kept separate to highlight point at which that component enters and leaves the process. Cyanide dissolution in the gold process is an example.
Common Waste Generation	A unit that generates a specific waste is not always the waste's point of exit from the process. It is necessary to ensure that the unit operation responsible for the nature of the waste is easily traceable in order to assist in process re-design and re-engineering. Thus it is important to couple waste generation with point of exit, for example linking leaching with filtration and thickening in the zinc circuit. Here the nature of the waste is determined to a greater extent by the leaching unit, than by the thickening and filtration units.
Energy Intensity	Energy generation has significant impacts on the environment; thus it is of specific concern. Within minerals processing significant amounts of energy are invested in order to overcome the entropy inherent in the very dilute raw materials entering the processes. There is always a balance to be reached between the purity of the product leaving a minerals processing plant and the amount of energy which it requires. Units with a high energy consumption must be identified. This is the reason for retaining smelting as a separate unit in the gold flowsheet (as opposed to collapsing it into calcining and smelting)

Data and information collation

Process flowsheets serve as a practical aide to the subsequent collection of all available and relevant data and information pertaining to the identified processes. In line with the extended system boundary outlined in Figure 2.2, process system data and information of key relevance in terms of the quantitative assessment of the environmental impacts associated with solid mineral wastes relates to factors of direct environmental significance (i.e. waste characteristics and management practises), as well as factors influencing waste characteristics (ore properties and processing information). The complete set of information requirements, and their relevance in terms of assessing solid mineral waste environmental impacts, is listed in Table 2.2.

Table 2.2: Summary of data and information requirements (shaded information fields indicate qualitative information)

	Information fields	Relevance in terms of assessing solid mineral waste environmental impacts
Ore characteristics		
General ore characteristics	Ore properties	Ore properties will influence waste characteristics, including composition and physical properties
	Environmental issues associated with ore/mining	
Process information	Mined volumes [Mt.yr^{-1}]	
	Ore management information	
Ore characterisation data	Mineralogical composition	
	Major element distribution[1]	
	Minor element distribution[1]	
Process Information		
Generalised flow diagram and processing information	Unit operations giving rise to solid waste streams	The unit operation from which the waste is derived will influence the physical and mineralogical properties of the waste
	Generalised processing information pertaining to dominant technologies, key operating parameters and related performance values	
Waste Characteristics and Management		
General waste characteristics	Waste properties	Generic and qualitative waste properties and related environmental issues will assist in the identification of key waste characteristics of potential environmental significance
	Potential to adversely impact environment	
Waste generation information	Production volumes [Mt.yr^{-1}]	The total mass of contaminants released may be considered a key characterisation factor and is needed for predictive modelling
	Solid to liquid ratio (S:L)	This parameter is needed for predictive modelling
	Particle size distribution (PSD)	The PSD is a property which is related to resulting environmental impact and is required for predictive modelling
Waste management information	Description of current management practice	Aspects of waste management are important to consider in assessing likely geochemistry and leachate predictive modelling
	Total yearly waste deposit area [m^2]	Required for predictive modelling
	% Area rehabilitated[2]	
	Moisture retained in waste [kg H_2O/kg waste]	Required for predictive modelling and to close a water balance around the deposit
	Rain ingress data [%][3]	
	Surface runoff data [%][3]	
	Evapo-transpiration data [%][3]	
Waste characterisation data	Mineralogical composition	Key significance in identifying key characteristics of environmental significance and in predictive modelling
	Major and minor element distribution[1]	
Liquid volumes co-disposed with waste	Volume of liquid effluent [Ml.yr^{-1}]	Required for predictive modelling as this can affect the quality and rate of leachate generation
	Quality of liquid effluent	Required for predictive modelling as this affects the quality of leachate
Empirical results from laboratory and field studies	Various experimental results from conventional leachability, acid generating potential and sequential chemical extraction tests on waste material Field studies on the compositions of solid waste materials and pore waters in a disposal scenario	Assists in the identification of key waste characteristics of potential environmental significance; enables first-order prediction of potential environmental impacts and liabilities.

[1] The elements listed in the major element distribution are those elements that make up the bulk of the solid waste in terms of major phases present. Minor elements are those elements present in smaller quantities in the waste – often trace elements,

which are of environmental significance

[2] The % area rehabilitated is that fraction of the total waste deposit area which is rehabilitated, often through renegotiation. This quantity may be time-dependent.

[3] These values are expressed as percentages of total annual rainfall

[4] TCLP or Toxicity Characterisation Leaching Protocol is a standard used to determine the potential leachability of solid wastes

2.1.2 Establishing a solid waste inventory database for the South African mineral-based resource industries

On the basis of the data and information requirements identified in the previous sub-section, a solid waste inventory database has been developed for the South African mineral-based resource industries, comprising generalised flowsheets and information spreadsheets containing information on ore characteristics, ore processing information and waste characteristics (see Table 2.2).

Scope of the inventory database

In order to define the scope of the inventory, it is first necessary to clarify what is meant by the South African minerals industry in this context. The South African minerals industry can be divided into a number of sectors, namely: coal, ferro-alloys, gold, mineral sands, non-ferrous metals and platinum group metals. In the main these sectors are characterised by a complex network of mining, ore production and processing, resulting in a number of intermediate products that are either exported or become inputs to downstream processes. To minimise difficulties in terms of analysis and data collection as a result of such process integration, the boundary of the mineral waste inventory has been set to include only primary products from ore processing. Thus, miscellaneous wastes arising from the manufacture of speciality products, such as commodity chemicals, are not included in the inventory. The exclusion of these wastes can be justified in light of the fact that the flows of these wastes were found be small in comparison to the wastes generated from upstream ore mining and primary processing. In addition, diamond mining and quarries fall outside the boundary as they do not produce a mineral or metal value, even though they do fall under the ambit of the South African Department of Minerals and Energy.

The starting point for the development of this inventory database is the Life Cycle Inventory (LCI) model, developed by Stewart (1999) as part of her doctoral thesis and summarised in a recent publication by Stewart & Petrie (2006). In its current form, however, the LCI databases, and the process flowsheet models that underpin them, generally only consider the route of the targeted metal and major components, or groups thereof, from the ore through to products and wastes for industry sectors (consistent with the conventional “cradle-to-gate system boundary). In order to deliver the information required by the subsequent steps in the proposed methodology for the assessment of the potential water and land-related impacts associated with resource-based process operations, this LCI model requires expansion of the system boundary and information databases beyond a consideration of averaged performance on an input-output basis supported by technology heuristics. Specifically, the inventory of solid mineral wastes also needs to take into consideration waste characteristics, waste management strategies, and the behaviour of contaminants in the local environment. Furthermore, an assessment of the environmental impact of solid waste disposal would not be complete without consideration of the fate and speciation of the constituent salt-forming elements and trace metals during ore formation, processing and waste disposal.

As an extensive data collection exercise was considered to be beyond the scope of this particular project, expansion of the existing LCI database was limited to information which is readily available (i.e. data and information that has already been collected and is thus available “in-house”). The key focus of this particular project task was thus to establish generalised flowsheets for the various local minerals processing industries, and to provide a consistent spreadsheet template to which data can be readily added as it becomes more available. Such a template also serves to make currently available data more accessible and comparable, and enables data gaps and deficiencies to be clearly identified.

The existing database can be viewed in Microsoft Excel, and accompanies this document on CD. In addition, Appendix A of the document contains generalised process flowsheets – together with tables summarising current data gaps and quality considerations, as discussed below.

Data availability and quality

Table 2.3 provides a general assessment of the data and information as collated within the existing database. Further details pertaining to the availability and quality of data for the individual industry sectors and sub-sectors are provided in Appendix A.

Table 2.3: Assessment of current mineral waste inventory data and information

Information field	Information assessment
General ore characteristics, process information and ore characterisation data	Ore properties: - Data is generally lacking as available resources tend to focus on the process with little attention given to the ore body. There is also limited information on waste rock characteristics, as these too are a function of local geology.
Generalised process flowsheets and information	The flowsheets of Stewart (1999) were taken as a starting point and other more detailed references were consulted in order to improve the resolution of these flowsheets with respect to waste management and disposal options.
General waste characteristics	Qualitative waste properties: - This information stems largely from in-house knowledge and familiarity with both the processes under consideration and the wastes generated - Qualitative waste properties may also be inferred from an analysis of relevant quantitative data Potential to adversely impact environment: - Primarily the generation and migration of leachate is a concern, although solid waste deposits may give rise to other environmental impacts.
Waste generation information	Production volumes [Mt.yr^{-1}]: - Total values widely available. Here, the production volumes were taken from the inventory of Stewart (1999). Where possible these values were updated with the 2002/2003 production figures (DME, 2003). - Difficulty obtaining split between waste handling options (e.g. dry dust vs. scrubber sludge) Solid to liquid ratio (S:L): - Information was obtained from the mass balances of Stewart (1999). - Information regarding liquid waste streams used to condition solid waste streams or for dust suppression is largely unavailable. Particle size distribution (PSD): - Particle size distribution information is not readily available and is only present in the inventory for a limited number of solid wastes. This information was obtained from reports detailing commissioned waste characterisation studies.
Waste management information	Description of current management practice: - This information is particularly difficult to obtain, as waste management strategies are particular to each plant and each waste type within the sub sector - Quantitative aspects are often not recorded in accessible documentation and may only be known to the on-site environmental manager. Furthermore, this information is perhaps even more difficult to obtain for older waste deposits, as there is often little historical waste management data and wastes may have been co-disposed complicating matters. Newer deposits are likely to be better managed with better records of waste disposal practices
Waste characterisation data	This information is typically determined through appropriate waste characterisation tests and chemical analyses. The data contained in the mineral waste inventory was obtained from various reports detailing such waste characterisation studies. Less detailed composition data was obtained from Stewart (1999).

Liquid volumes co-disposed with waste	Volume of liquid effluent [Ml.yr^{-1}]: - In the inventory, the volume of liquid co-disposed with the solid wastes was taken from the mass balances of Stewart (1999). However, additional liquid wastes used, for example, for conditioning and dust suppression are not recorded. Quality of liquid effluent: - The composition of any liquid waste streams is also plant specific and may vary with time. The quality of these streams, if assessed, will form part of a waste monitoring strategy.
Results from leachability studies	This information is not currently available for most of the wastes. This is because this information is obtained from specialised, commissioned reports investigating the leach behaviour of the waste.

As it currently stands the database is largely incomplete and the quality (including detail, consistency and reliability) of available data generally poor. As already discussed in the previous section, the information contained in this database has been purposefully limited to readily available in-house data and information, and it is thus recognised that there is still scope to add to this database through further data collection efforts. Although some of this data will be available in the published literature (e.g. academic journals and reference books), much of the available knowledge is grounded in in-house experience and documents, and thus lies within the minerals industry as well as industry-related service and research organisations. Discussions in the previous chapter of this report (Section 1.1.2) have, however, indicated that such knowledge is presently limited, particularly in terms of the minor and trace compositions of input-output streams. Furthermore, data is seldom determined to the level of detail and/or certainty required for accurate and reliable impact assessment predictions. Hence, even with the best data collection efforts, the mineral waste inventory database is likely to remain incomplete and characterised by high data uncertainty.

It is these data gaps and deficiencies that the following steps (i.e. qualitative and quantitative waste characterisation) of the proposed methodology aim to address.

2.2 Qualitative Waste Characterisation: Step 2

Qualitative characterisation is the second step in the proposed methodology for the quantitative assessment of solid waste impacts. This step essentially serves as a screening assessment, by generating preliminary information on the environmentally significant characteristics of solid wastes from the primary mineral-based resource industries.

The conceptual approach proposed for the first-order prediction of solid mineral waste characteristics, of key significance in terms of potential environmental impact, is outlined in Figure 2.3. This approach, developed by Broadhurst (2006) as part of her doctoral thesis, essentially entails addressing current data gaps and deficiencies through reconciliation of available empirical data with a fundamental understanding of element properties and distribution behaviour in two systematic and consecutive steps. In the first instance, solid waste characteristics are predicted from a consideration of ore type and composition (i.e. waste source), combined with knowledge of the process route from ore to waste (i.e. waste origins). The second step entails the prediction of key characteristics relating to criteria of environmental significance, namely hazard potential and mobility of the elements.

Figure 2.4 illustrates the relevant inter-relationships between the feed ore characteristics, ore processing operations, waste output compositions, waste component properties and, ultimately, environmental impacts.

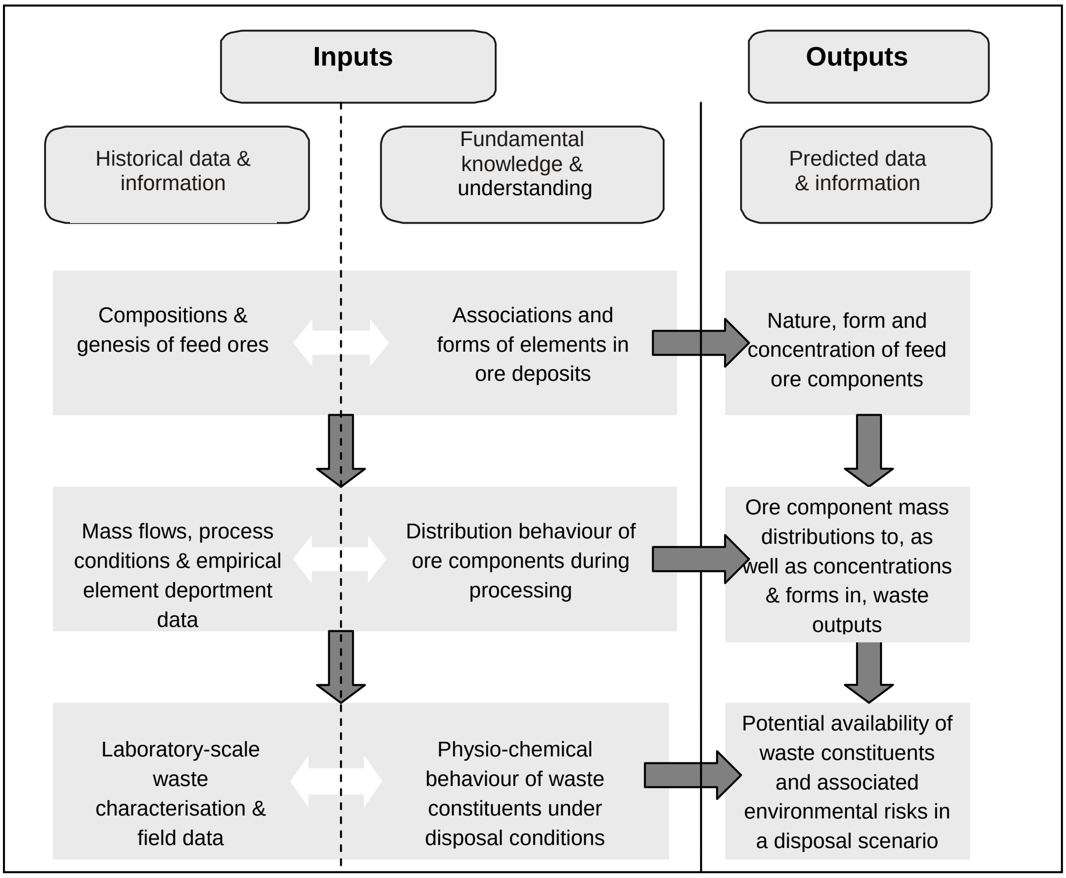


Figure 2.3: Conceptual approach for the prediction of key solid waste characteristics on the basis of origins and source

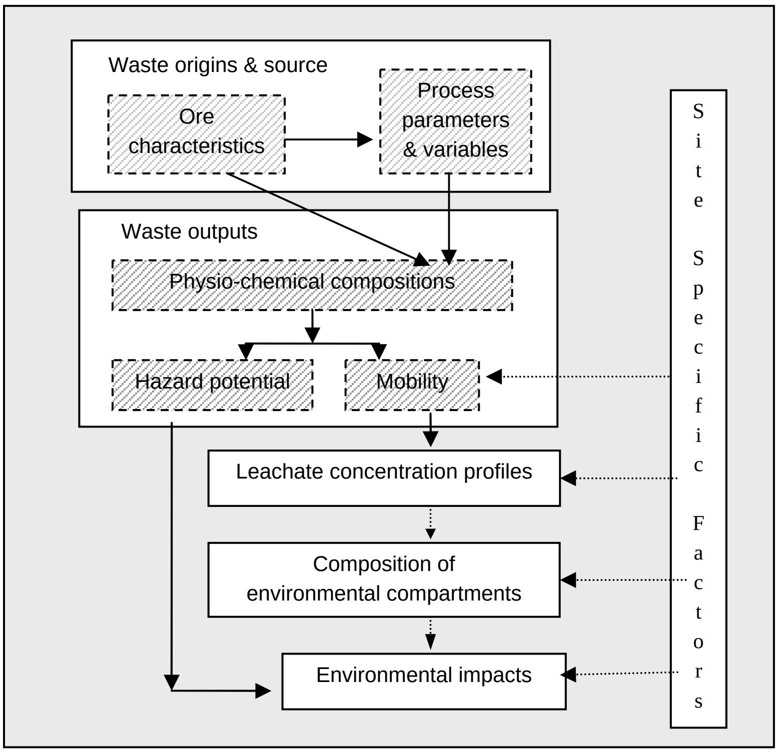


Figure 2.4: The ore → waste → leachate→ environmental impact chain (the shaded areas and solid lines represent the steps of significance in terms of the qualitative waste characterisation step)

2.2.1 Predicting physio-chemical waste characteristics on the basis of origin and source

The identification of solid waste constituents of key significance in terms of potential environmental risk requires prior knowledge of both their concentrations and forms. Due to their relevance in terms of technical and economic criteria, such as product quality and operational throughput, the behaviour of the targeted metal and major ore components in ores and beneficiation input-output streams is generally fairly well understood. Data gaps and inconsistencies pertaining to these ore components can, for the most part, be adequately addressed on the basis of meaningful generalisations and simple mass balance calculations. In contrast, available data and information relating to compositions of trace and minor co-elements is largely qualitative and inconsistent, and their deportment during the formation and subsequent beneficiation of ore deposits generally less well understood. The generalised strategy for predicting physio-chemical compositions of solid mineral wastes, developed by Broadhurst (2006) as part of her doctoral thesis and summarised in a recent conference paper (Broadhurst et al., 2006), is presented in Figure 2.5.

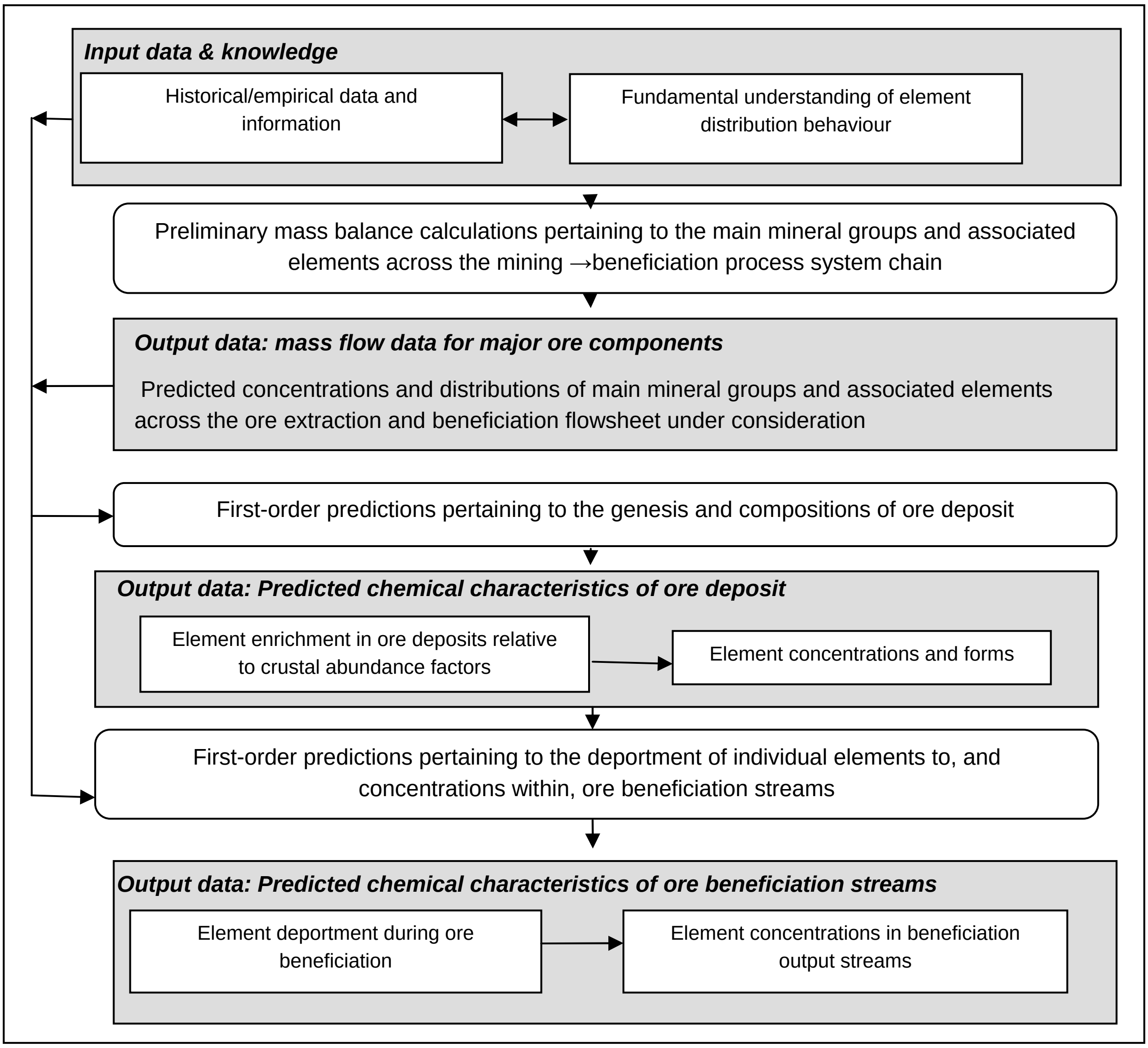


Figure 2.5: Generic procedural framework for predicting the chemical characteristics of ore deposits and beneficiation streams

This strategy is largely underpinned by – and relies to a significant extent on – a fundamental understanding of the key factors controlling the chemical properties, distribution behaviour and associations of elements within ore deposits and processing reactor units. This understanding forms the basis for the development of generic criteria for the theoretical prediction of the potential distribution factors, concentrations and forms referred to in Figure 2.5. The theoretical data and information is then reconciled or "harmonised" with available empirical data to generate a comprehensive and quantitative list of potential element distribution factors which, when combined with total mass flow data, results in a first-order inventory of process input-output stream compositions. The key criteria and qualitative information pertaining to element distribution behaviour within mineral deposits and during subsequent ore processing operations are summarised in Figure 2.6 and Table 2.4 respectively. This information was derived on the basis of a comprehensive review and assessment of the literature pertaining to the formation and classification of metal-bearing mineral deposits (see for example Battey, 1981; Corrins, 1969; Cox, 1995; Niggli, 1954; Thornton, 1983) and their subsequent processing (e.g. Bridge, 2000; Canterford, 1985; Flett et al., 1996; Habashi, 1982; Hayes, 1985; Kelly & Spottiswood, 1982; Mitchell, 2000; Moore, 1990; Roberts et al., 1971; Rosenqvist, 1983; Rubenstein & Barsky, 2002; UNIDO, 1987; Warhurst, 2000; Wills, 1997) – as well as the fundamental principles of mineralogy, geochemistry and inorganic chemistry.

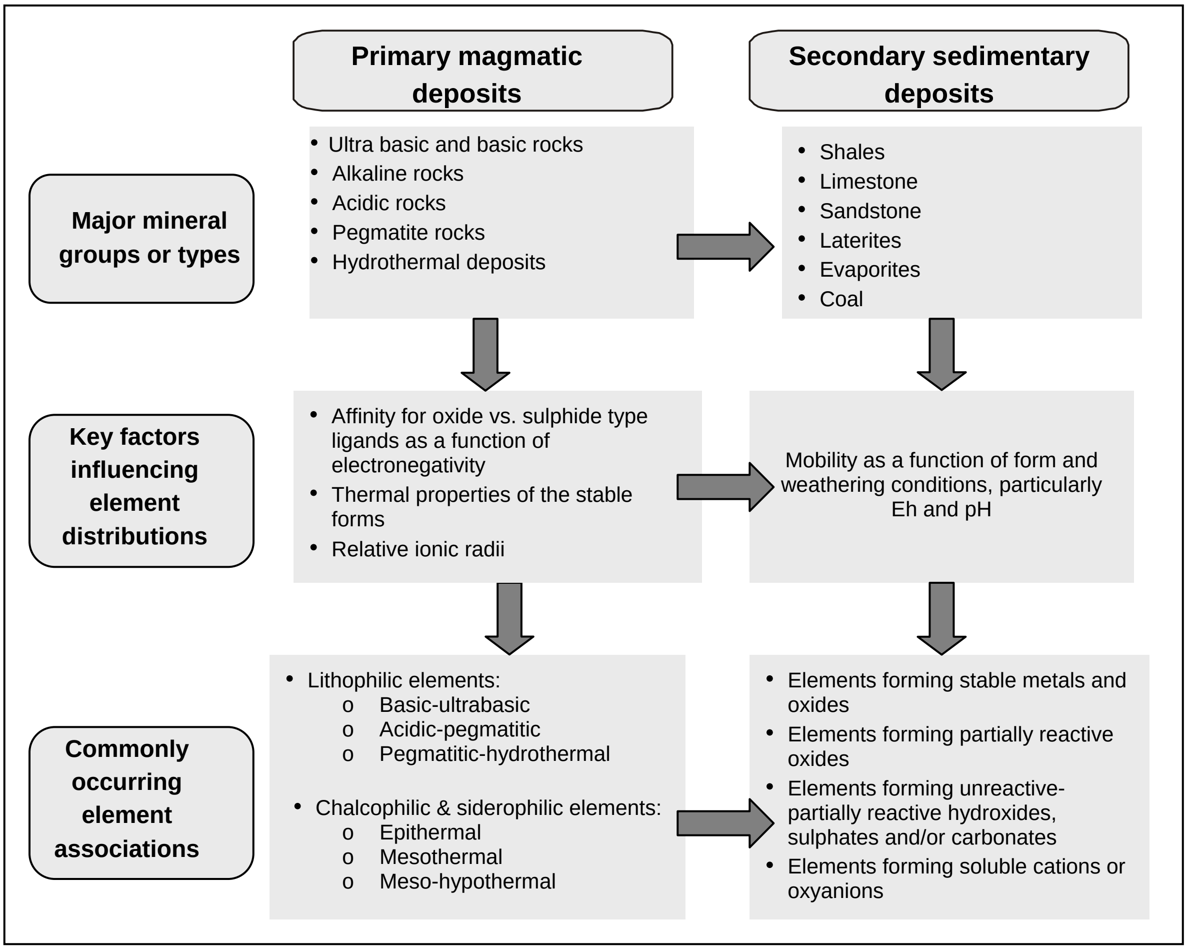


Figure 2.6: Summary of element distribution behaviour and associations within mineral deposits

Table 2.4: Summary of generic solid waste characteristics and influencing factors as a function of process unit operations and related operating parameters

Waste type	Generic characteristics	Process related factors influencing element distribution
Mining/Ore extraction		
Waste rock or overburden	Crushed porous rocks comprised of gangue minerals as major components.	Ore characteristics
Concentration		
Tailings	Finely ground (typically < 1mm) and wet (typically 55-65% moisture). Comprised mainly of gangue minerals (including host rock and sub-economic ore-bearing minerals)	Classification: grain size; Gravity separation: density and size; Heavy medium separation: density; Magnetic separation: magnetic susceptibility; Electrostatic separation: electric conductivity; Froth flotation: surface chemistry (wetability)
Hydrometallurgical extraction		
Vat leach residues	Finely divided & wet (typically 10-20% moisture)	Mobility of elements under leaching conditions, particularly pH, Eh and nature of the leachant
Heap/dump leach residues	Crushed ore similar in composition to feed ore, with traces of residual leach reagent	
Effluent treatment residues	Finely divided synthetic salts, frequently amorphous (typically 20-50% moisture content). Normally relatively small volumes, but high metal/metalloid content in comparison to leach residues	
Metal recovery slimes/ sludges	Semi-gelatinous colloids of suspended material, normally with high metal/metalloid content. Relatively small volume, but high metal/metalloid content	
Pyrometallurgical extraction		
Smelter slags	Large particles of glassy material, comprised mainly of oxides and silicates of major elements (Ca, Mg, Al, Fe), with isomorphic trace-minor metals. Physical characteristics such as particle size & porosity dependant on cooling methods	Stable element forms and related viscosities as a function of smelting conditions, particularly temperature, redox conditions and additives (fluxes etc)
Smelter flue dusts	Fine particles (0.5 -10µm). Generally comprised of significant quantities of oxidized slag and feed ore, with fine (< 1 µm) condensed volatiles on particle surfaces. Can be dry to wet (up to 65% water). Mass flows dependant on extent of solids blow-through which is related to furnace technology and feed particle size	Stable element forms and related volatility's as a function of smelting conditions, particular temperature and redox conditions
Metal refining effluent treatment residues & slimes	As for hydrometallurgical effluent treatment residues	As for hydrometallurgical effluent treatment residues

2.2.2 Screening of environmentally significant solid waste characteristics

The second stage of the proposed approach for the qualitative characterisation of solid mineral wastes entails the prediction of key characteristics relating to criteria of environmental significance. This is consistent with tiered environmental performance assessment approaches, in which screening assessments are applied in the first instance to identify the significant issues, alternatives and decision points, for which more detailed and accurate assessments are warranted or required (see discussions by DWAF, 2002; EEA, 1997; Lawrence, 1997; Noble, 2000 & 2002; Wentzel, 1999). Such an approach is particularly appropriate for evaluating complex systems in the early stages of a project life cycle, as it recognises that not all substances in a waste stream raise the same level of concern with respect to their environmental impact, and focuses attention on those wastes and/or elements with the potential to present a significant risk to human health and the environment.

The prior identification of potentially strategic constituents, particularly trace to minor metals, is in fact considered to be a vital and integral part of predicting environmental impacts associated with solid wastes from the primary mineral-based resource industries (see discussions by Hansen, 2004). This is because such wastes generally contain a multitude of contaminants, and it is clearly neither practical nor desirable to develop separate indicators, such as the impacted land footprint indicator developed by Hansen (2004), for each of these. Whilst consideration of TDS, rather than individual salt ions, is appropriate for defining a salinity footprint, the same approach cannot be applied to metals. This is due to the fact that there is significant overlap between impacted land footprints predicted for different metal species and adding these footprints together to obtain an indicator would therefore suggest a far greater land area impacted by metals than in reality. An alternative approach is thus required to reduce the number of metals footprints necessary to define an impacted land footprint indicator for metals. In accordance with the approach proposed by Hansen (2004), this is achieved by identifying environmentally significant or “strategic” metals. An impacted land footprint indicator based on these strategic metals can be assumed to encompass other metal footprints, and hence be representative of the environmental impact of all metals contained in the waste.

Screening environmental performance assessments generally entail the use of simple “ranking and scoring” methodologies based on generic and readily measured environmental risk criteria or indicators. Existing ranking and scoring systems have, however, been developed specifically for prioritising risks and impacts associated with pure chemical substances, mainly organic, on the basis of criteria such as their mass, toxicity, persistence and, in some cases, solubility (see discussions by Cano-Ruiz & McRae, 1998; Hertwich et al., 1998; Pennington & Yue, 2000; US EPA, 1989), and are generally not suitable for evaluating and prioritising the environmental risks associated with metal-bearing solid wastes from mineral-based resource industries. A review and assessment of the general literature has indicated that the criteria of key significance in terms of evaluating and prioritising the environmental significance of typical solid mineral waste constituents can be broadly categorised as those factors influencing the hazardous nature of the waste constituents, as well as their availability for release to the environment in a disposal scenario. The key criteria identified through this study are summarised in Figure 2.7.

On the basis of this understanding, a methodology algorithm has been developed, in which those constituents which are unlikely to be of environmental significance are excluded from further and more detailed investigations in a step-wise and relatively simple, yet scientifically valid, manner. This methodology, developed by Broadhurst (2006), is summarised by the procedural framework in Figure 2.8. Detailed equations for the calculation of hazard and risk potential factors are presented in Appendix B.

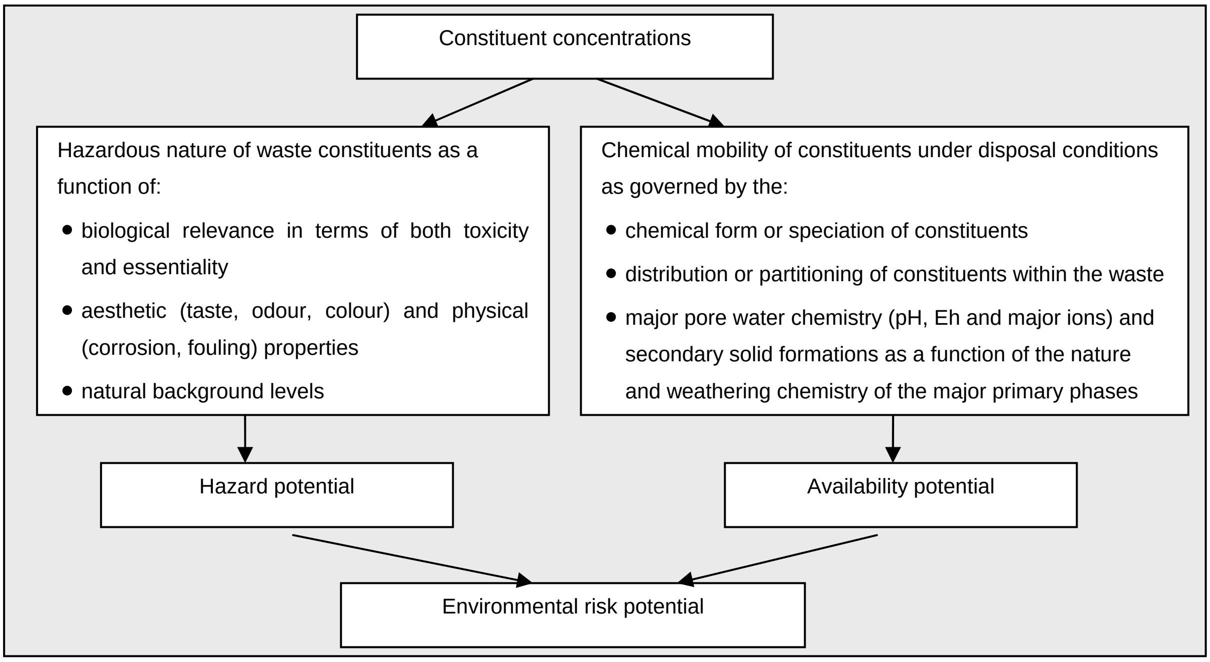


Figure 2.7: A summary of environmentally significant solid mineral waste properties and governing criteria

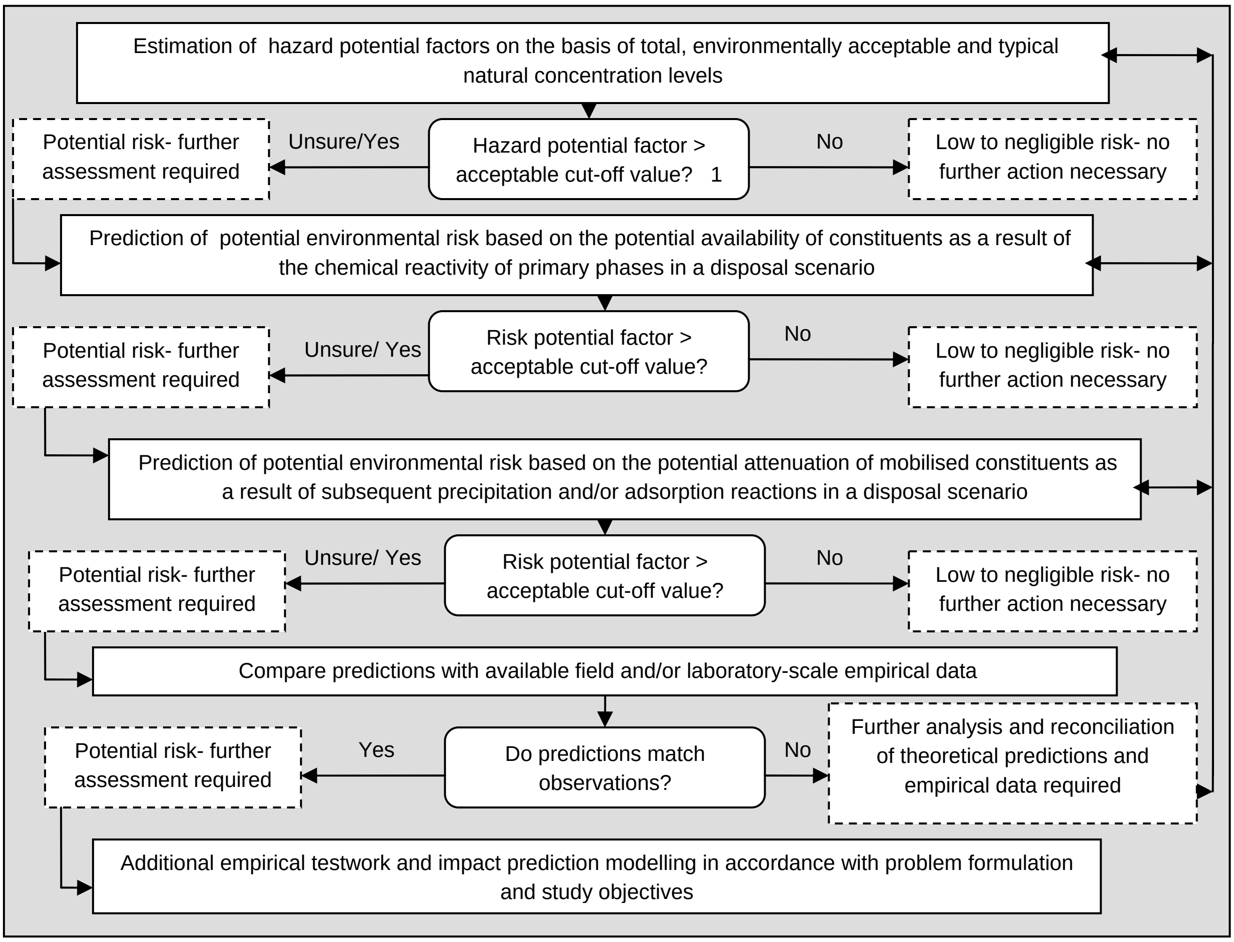


Figure 2.8: Procedural framework for the screening of potentially strategic constituents in solid mineral wastes

2.3 Quantitative Waste Characterisation: Step 3

The third step in the methodology to predict impacts from solid mineral wastes is quantitative waste characterisation. Besides providing information and data necessary for both conceptual and numerical leachate generation model development, this step also allows the qualitative waste characterisation models (Step 2) to be validated, and contributes to the mineral waste inventory (Step 1) by filling data gaps. This is represented by the feedback loop in Figure 2.1.

Conventional quantitative waste characterisation relies largely on the application of empirical methodologies to derive data pertaining to the chemical compositions, physical properties and the leach behaviour of solid wastes under laboratory-scale test conditions. Whilst a vast number of empirical methodologies have been developed for the characterisation of solid wastes, the bounds of uncertainty and inefficiency associated with currently available waste characterisation techniques remain high (see discussions in Chapter 1, Section 1.1.2). There is thus a need to improve the way in which solid mineral wastes are characterised, in terms of both the general approach, and in the design and interpretation of empirical methodologies. In recognition of this, a systematic and informed approach to the quantitative derivation of waste characterisation data, to specifically support subsequent predictive modelling, has been developed in partial fulfilment of the overall project objectives. This approach is underpinned by a fundamental understanding of the leach behaviour of solid mineral wastes in a disposal scenario (Section 2.3.1), as well as the consequences and limitations of the available waste characterisation methodologies (Section 2.3.2). Together, this knowledge and understanding forms the basis for the development of a conceptual empirical solid waste characterisation procedural framework (Section 2.3.3), which can be tailored to accommodate various waste types and disposal scenarios.

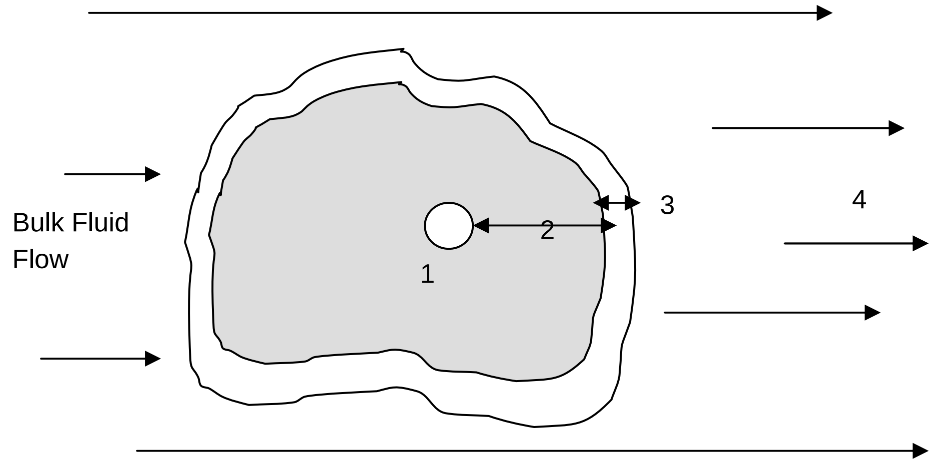
2.3.1 The leach behaviour of solid mineral waste: an overview

In order to understand the interaction of all the factors influencing the time-dependant leachate concentration profiles, consideration first needs to be given to the fundamental principles behind the release of contaminants from typical mineral waste deposits. This, in turn, provides a basis for evaluating the various waste characterisation tests in terms of how they reflect the leach behavior and influencing factors in the field, and how the results can be expressed mathematically in a predictive model.

Whilst the hazard potential of a specific solid waste constituent is largely specific or inherent to a particular chemical species, the release of such constituents from a waste deposit site is governed by a complex network of chemical reaction and physical transport mechanisms, occurring on both the particle and bulk deposit level. As discussed in detail by Cohen et al. (1999), most solid waste particles are porous, enabling the bulk liquid to diffuse into particle pores and the aqueous environment to be extended throughout the solid particle. Reactants and dissolved chemical species are thus able to enter and leave the pores by diffusion transport, commonly termed intra-particle diffusion. Chemical reactions also occur on the surfaces of the particles, with the mass transfer of reactants and chemical contaminants between the surface and the bulk liquor also occurring by molecular diffusion. In short, the mechanisms governing release of contaminants from a solid waste deposit can be summarised in a number of steps, as illustrated diagrammatically in Figure 2.9. The rate and extent of leaching, and the governing mechanisms, will, furthermore, be dependant on a number of inter-related factors, pertaining to both waste- and site-specific characteristics.

Clearly, the availability of a contaminant for release to the surrounding environment is governed in the first place by their chemical reaction with the liquid or gaseous reactants within the pores, or on the surfaces, of the solid waste particles. In accordance with the general literature (Bourg, 1995; Eary et al., 1990; ICME, 1995; Jones, 1995; OECD, 1993; Parametrix, 1995), the main reaction mechanisms and parameters controlling the mobility of solid waste constituents include:

- dissolution/precipitation reactions, which are largely controlled by pH; *and/or*
- oxidation/reduction reactions, which are largely controlled by Eh; *and /or*
- adsorption/desorption reactions, which are controlled by a number of inter-related factors, including the ionic charge of the element being adsorbed; pH and ionic strength of the solution; and the surface properties of the adsorbing solids



Step 1 Chemical reaction: The mobilisation of contaminants from solid waste deposits can occur via a number of chemical reaction mechanisms.

Step 2 Intra-particle diffusion: Reacting species are transported to, and mobilised solid species from, the site of reaction through the particle pores of the solid by means of molecular diffusion.

Step 3 Mass transfer: Particle surface - bulk liquid inter-transfer of reacting species and mobilised solid species occurs by means of molecular diffusion.

Step 4 Bulk liquid transport: The mobilised species are transported through the bulk deposit, either by molecular diffusion through stagnant liquor phases, or by convective transport in a moving fluid front.

Figure 2.9: Overarching mechanisms describing the leaching of solid waste constituents (Cohen et al, 1999)

These reactions and influencing parameters are, in turn, related to a number of waste-specific properties, the main ones being:

- *Total constituent concentration*: In accordance with the basic laws of thermodynamics, the chemical reactions controlling the mobility or availability of any particular constituent will be dependant on its total concentration.
- *Chemical form or speciation of constituent*: The chemical forms of the constituents in the solid phase can strongly influence their chemical properties and leaching behaviour, as well as their toxicity.
- *Distribution of constituent within the waste*: The distribution or partitioning of a specific element in the solid phase can be important for controlling both the extent and rate of leaching. Elements or mineral phases that are enriched on particle surfaces will be more accessible to solution, and consequently leached initially at more rapid rates than elements that are distributed more uniformly within the waste matrix. Elements that are incorporated predominantly in sparingly soluble phases will be released to solution only as fast as these solids dissolve, assuming congruent dissolution. In

many cases, elements that are physically adsorbed onto the surfaces of major phases or present as carbonate/hydroxide precipitates may only become available if the natural properties of the waste solutions (leachate), particularly pH and ionic strength, change as a result of weathering or microbial activity within the waste deposit.

- *Physical properties:* Physical characteristics, such as degree of saturation, bulk density and porosity, will determine the rates of liquid flow and ultimately influence the rate at which constituents are released to the surrounding environment.
- *Compositions and weathering chemistry of major phases in the waste*: Alterations to major phases as a result of weathering or microbial activity can influence the availability of trace to minor constituents and the nature of leachate generated, through various pathways. These include:
    - Changes in the major properties of the pore solutions or leachate in contact with the solid particles, particularly in terms of pH, redox potential and major ion concentrations. As discussed in the previous section, such changes can have a significant effect on the mobility of waste contaminants, particularly where this is controlled by solubility, redox speciation or sorption reaction mechanisms. pH, in particular, is considered to be the master variable controlling the leachability of metal species from solid mineral wastes (Jones, 1995), influencing almost all chemical processes controlling the availability of waste constituents. pH changes in the pore solution due to chemical and/or microbial weathering of major phases over both the short and the long-term is thus a critical aspect of the chemical behaviour of solid wastes.
    - Formation of secondary major phases which can adsorb minor and trace elements.
    - Liberation of trace elements incorporated in the structure, or bound to the surface, of major phases.

  In many cases the chemical reactions governing the weathering of major phases, such as the dissolution of silicate mineral phases, carbonation of the pore waters and air oxidation of pyrite, are slow, incomplete and irreversible, and will thus continue to influence the major pore water chemistry and mobility of trace to minor elements over extended time periods. According to Hansen (2004), the time taken for complete oxidation of pyrite in a waste dump of less than average height (10m), will typically be in the order of 200 to 500 years. It is not surprising then that researchers such as Jones (1995) have reported that the nature and chemical behaviour of the major phases in a disposal scenario, and the subsequent formation of secondary solids, is the major factor influencing the release of minor metals from solid wastes, and hence the leachate compositions, over the long-term.

Based on this understanding, a conceptual model summarising the chemical behaviour and influencing factors governing the release of solid mineral waste constituents in a disposal scenario has been constructed, and is presented in Figure 2.10. In accordance with this model, the chemical mobility of solid mineral waste constituents in a disposal scenario will be determined in the first place by the stability or reactivity of the primary mineral phases as a function of environmental conditions within the deposit (mainly redox potential, oxygen concentrations, microbial activity and pH), and in the second place by the extent of attenuation of the solubilised constituents through precipitation/dissolution and adsorption/desorption reactions. These attenuation reaction mechanisms are generally rapid, fully reversible equilibrium-controlled reactions, which are dependant on a number of parameters, including constituent activity, redox potential, the nature and concentration of major soluble ions and secondary solids, and, in particular, pH. In contrast, the rates at which the primary phases are weathered or altered can vary quite considerably, ranging from rapid equilibrium-controlled reactions, resulting in short-term mobilisation of associated elements, to slow kinetically-controlled reactions, which are only likely to result in significant mobilisation in the medium- to long-term. In some cases the weathering reactions may be so slow that they do not result in any significant mobilisation of elements within the time frame of consideration and can therefore be discounted (Brown et al., 2000).

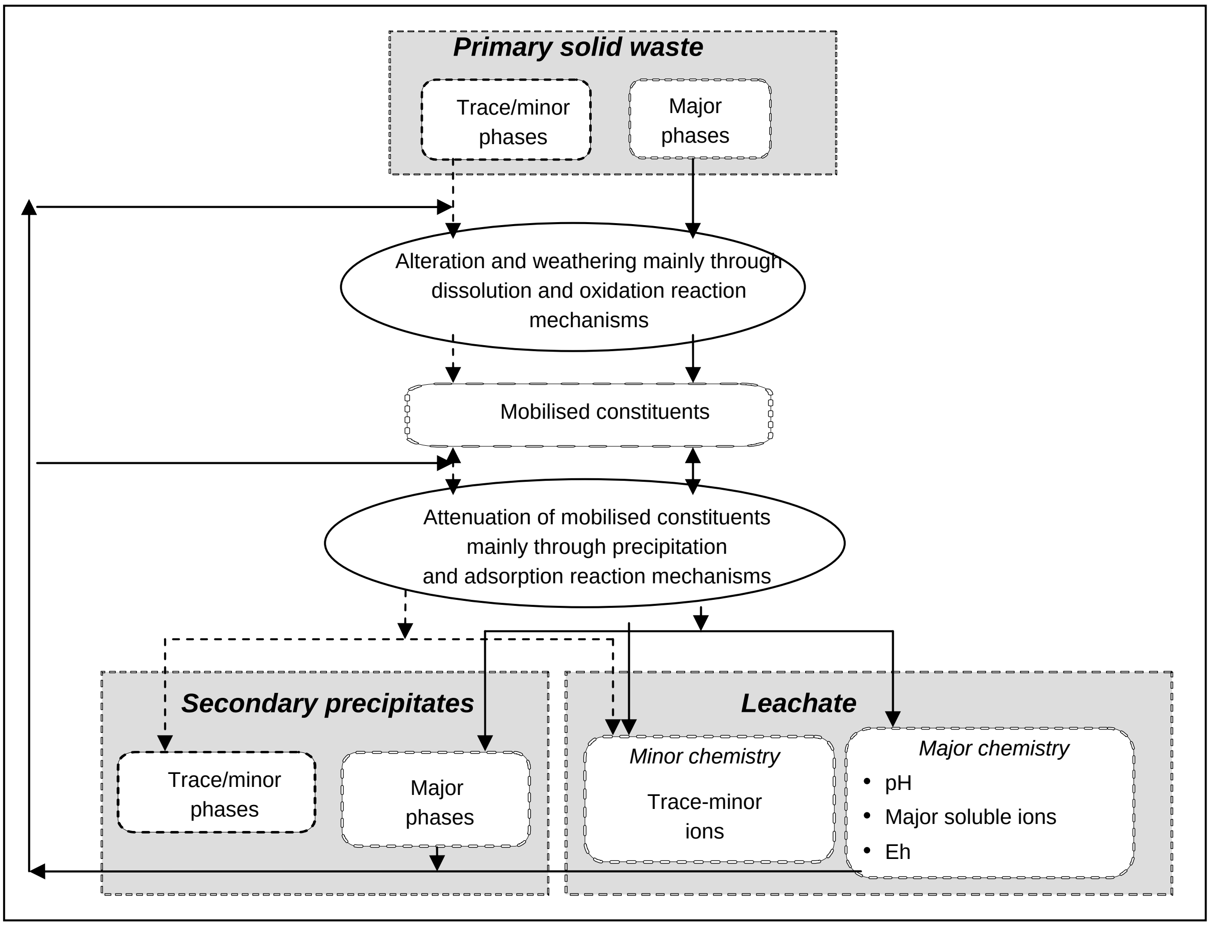


Figure 2.10: Conceptual model of the chemical behaviour of solid mineral waste constituents

2.3.2 Overview of current waste characterisation tools.

A number of laboratory-scale tests have been developed for the characterisation of solid wastes, the most commonly applied ones of which are summarised and assessed in Tables 2.5 and 2.6 overleaf. As indicated in Table 2.6, each of these empirical waste characterisation methodologies has its limitations, and is specifically designed to reveal only one or two aspects of the properties of the solid under investigation.

In general, the characterisation of solid wastes can be based on a number of criteria including chemical compositions, physical properties, and leach behaviour. Of these characteristics, it is, however, the leach behaviour which is considered to provide the most pertinent information in terms of potential environmental availability and impacts of solid waste constituents, and which has been the focus of both industry and legislative bodies. Laboratory-scale leach tests are, however, only capable of providing a partial picture of the time-dependant release of contaminants in a disposal scenario. In the first instance empirical leachate extraction tests cannot adequately simulate the physical transport processes, including the non-ideal fluid flow and gas diffusion mechanisms, occurring in a full-scale deposit. Furthermore, as discussed in the previous sub-section of the report, many of the key reaction mechanisms controlling the leach behaviour of major phases in solid minerals wastes are extremely slow, and consequently the dominant chemistry of the pore solutions (pH, Eh and ionic strength) cannot be simulated in short-term leach tests.

Table 2.5: Description of empirical solid waste characterisation methodologies and techniques

Test Description	Primary outcomes	Examples	Useful references
Analytical & static empirical methodologies			
Physical properties	Quantitative data on physical properties (e.g. density, particle size, and porosity)	Particle size: laser diffraction, PCS (Photon Correlation Spectroscopy), infrasizing, cyclosizing, screening; Density: helium pycnometer; Total pore volume and pore size distribution: mercury porosimeter; Surface area and pore size distribution: BET (Brunauer-Emmet-Teller) analyser	
Total element analysis	Quantitative data pertaining to the concentration of individual metals/semi-metals, carbonate & sulphur species	X-Ray Fluorescence Spectrometry (XRF); Atomic Adsorption Spectroscopy (AAS);Inductively Coupled Plasma (ICP) techniques; LECO analysers; wet chemical techniques	Lapakko (2002)
Mineralogical analysis	Qualitative and/or quantitative data on the forms and distribution of contaminants	X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), optical microscopy	Boer & Pinetown (2006), Bruckard & Woodcock (2004), Buchter et al. (2004)
Sequential chemical extraction tests	Quantitative information on the partitioning or distribution of trace to minor elements in major phases	Various	Carlsson et al. (2002), Coetzee et al. (2006), Dang et al. (2001), Dold & Fontbote (2001), Dold (2003), Fanfani et al. (1997), Guirco et al. (2000), Jaebong (2003), Kontopoulous et al. (1995), Leinz et al. (2000), McGregor and Blows (2002), Mitchell et al. (1994), Ribet et al. (1995),van Herck & Vandacasteele (2001
Tests for acid generating and/or neutralising capacities	Quantitative information on the capacity of a waste to generate or neutralise acid.	Acid Base Accounting (ABA) or Net Neutralisation Potential (NNP); Net Potential Ratio (NPR); Net Acid Producing Potential (NAP); Net Acid Generation (NAG) test	Lapakko (2002), Miller et al. (1991), Paktunc (1999), Skousen et al. (2002), Sobek et al. (1978), Strőmberg & Banwart (1999), US EPA (1994), Usher et al. (2003A & B), Weber et al. (2004)

Table 2.5 continued…..

Test Description	Primary outcomes	Examples	Useful references
Laboratory leach tests			Eary (1990), Environment Canada (1990), Fällman & Aurell (1996), Jones (1995), OECD (1993), Stegemann & Cote (1990), Twardowski & Szczepanska (2002), van der Sloot et al.(2003a), van der Sloot et al. (2003b), van der Sloot & Dijkstra (2004), Whalstrő́m (1996).
Single batch extraction tests under standard conditions	Quantitative data on contaminant availability under specific test conditions.	Toxicity Characteristic Leaching Procedure (TCLP) of the US EPA; German Din Water Leach Tests; South African Acid Rainfall Leach Procedure (ARLP)	
Parallel batch extraction tests under variable conditions	Quantitative data on contaminant availability as a function of leach conditions	EC CEN pH-stat test PREN 14429,	
Serial batch tests	Quantitative data on changes in contaminant availability with time	NEN 7341: 1995; NEN 7349:1995; PREN 12457-3	
Concentration build-up tests	Qualitative information pertaining to the effects of the build-up of contaminant concentrations in pore liquors	None available	
Flow-through tests	Quantitative data on changes in contaminant availability with time	Various (e.g. European PREN 14405)	

Table 2.6: Standard empirical waste characterisation methodologies: Interpretation and limitations of data/information outputs

Test description	Application & interpretation of data/information outputs	Specific limitations
Analytical & static empirical methodologies		
Physical properties	Model input data pertaining to fluid flow/leachate generation properties	
Total element analysis	To infer potential availability and environmental significance of contaminants, in conjunction with mineralogical information	Results are not representative of constituent availability
Mineralogical analysis	• To infer potential availability and significance of contaminants, in conjunction with element analysis • To infer potential phases and reactions controlling element release • To identify effect of chemical weathering or leaching on chemical properties	• Quantitative mineralogical analysis of complex systems can be time-consuming and costly • Methodologies are generally not sufficiently sensitive for identification & quantification of trace to minor element phases
Sequential chemical extraction tests	As above	Results can only be considered semi-quantitative unless validated.
Tests for acid generating and/or neutralising capacities	• To infer potential environmental risk in terms of acid drainage generation • To infer potential minimum pH value in leachate	Can be misleading due to highly time-dependant nature of pH profiles in the field.
Laboratory leach tests		
Single batch extraction tests under standard conditions	To infer potential availability and relative environmental significance over geological time	• Provide limited information in terms of chemical mechanisms and influencing parameters • Do not provide information on the time-related nature of contaminant release

Table 2.6 continued……

Test description	Application & interpretation of data/information outputs	Specific limitations
Parallel batch extraction tests under variable conditions	• To identify main types of chemical mechanisms controlling contaminant release under various disposal conditions • To identify controlling solid phases and derive quantitative reaction equations, in conjunction with thermodynamic analysis	• Cannot identify or quantify very slow, kinetically controlled reactions • Cannot simulate effect of low L/S ratios, and/or simulate low L/S disposal regimes • Do not provide information on the time-related nature of contaminant release
Serial batch tests	• To derive an estimate of the time-dependant concentration profiles, in conjunction with knowledge on field flow rates • To quantify maximum availability over geological time • To identify main types of chemical mechanisms controlling contaminant release	• Cannot identify or quantify very slow, kinetically controlled reactions • Cannot simulate effect of low L/S ratios, and/or simulate low L/S disposal regimes • Information too limited to identify controlling solids and reaction equations, or to assess effects of variable disposal conditions
Concentration build-up tests	To analyse effects of high ionic strength and saturated pore solution concentrations on contaminant availability	• Interpretation in terms of field conditions is highly uncertain • Results are unlikely to be applicable to high L/S disposal regimes
Flow-through tests	• To derive an estimate of the time-dependant concentration profiles, in conjunction with knowledge on field flow rates. • To quantify maximum availability over geological time. • To identify main types of chemical mechanisms controlling contaminant release • To derive quantitative data on hydrodynamic characteristics	• Cannot identify or analyse very slow, kinetically controlled reactions • Cannot simulate high L/S disposal regimes • Information too limited to identify controlling solids and reaction equations, or to assess effects of disposal conditions • Tests are time –consuming and complicated to set-up and run • Results tend to be erratic and inconsistent

In many cases these kinetically-controlled reactions will thus need to be inferred from fundamental considerations based on knowledge of the waste origins and source (i.e. from qualitative waste characterisation outcomes) and physio-chemical properties. Theoretical predictions of element distribution behaviours in mineral resource-based process systems can be also be conducted using equilibrium speciation models, which are designed to generate information and data on the equilibrium distribution of phases, as well as the chemical compositions of interfacing fluid-solid systems, on the basis of fundamental thermodynamic principles. Examples of commercially available thermodynamic models (also termed equilibrium speciation models or aqueous geochemical models) for aqueous systems include MINTEQA2 version 3.0 (Allison et al., 1990) and version 4.0 (US EPA CREAM, 2005); OLI (OLI Systems Inc, 1991); PHREEQE (Parkhurst, 1995); WATEQF4 (Ball & Nordstrom, 1991); ORCHESTRA (Meeussen, 2003); and HSC Chemistry® for Windows, version 5.1 (Outokumpu, 2002). Although equilibrium thermodynamic models do not take into account factors such as reaction kinetics and non-idealities (e.g. formation of mixed or non-stoichiometric precipitates), they can provide useful and versatile information in terms of the most likely stable forms and major distribution pathways of elements in process systems. This is particularly the case for the leachate generation processes occurring within solid mineral waste deposits, as most of the precipitation/dissolution and/or adsorption/desorption reaction mechanisms controlling the extent to which waste constituents are attenuated within solid waste deposits are rapid, equilibrium-controlled reactions. Furthermore, due to the extended time frames typically associated with mineral waste deposits, in many cases even the availability of elements present in the form of slow-reacting primary phases (e.g. sulphides) can be predicted on the basis of thermodynamic considerations alone. Thermodynamic models can thus play a valuable role in quantitatively predicting the environmental availability of solid waste constituents in a disposal scenario, as well as their speciation within the contaminated leachate, both of which are of significance in terms of potential environmental risk.

2.3.3 A generic procedural framework for quantitative solid mineral waste characterisation

On the basis of the review in Section 2.3.1, the waste-specific properties considered to be of key significance in terms of informing and supporting subsequent predictive models, and for which data and information needs to be derived, include:

- major phases and related reaction mechanisms controlling the major pore solution chemistry (in terms of pH, major soluble ions and Eh) and predominant secondary solid formation.
- major physical properties influencing liquid flows, particularly in terms of porosity, particle size distribution, saturation levels and density.
- potential environmental significance of trace-minor constituents, as well as the major soluble salt-forming and pH-controlling constituents, on the basis of their relative availabilities and hazard potential.
- solid phases and reaction mechanisms controlling the mobility of trace-minor elements as a function of pH and major soluble ion concentration profiles.
- time-related release of strategic contaminants under conditions simulating those in the field.

The limitations of the various waste characterisation methodologies (as discussed in the previous sub-sections), in combination with the inherently complex nature of the solid waste disposal system, means that the derivation of such information will require execution of a number of different characterisation methodologies, in the form of a systematic protocol. Effective waste characterisation will, furthermore, require that the design of such a protocol be based on a clear understanding of the limitations and attributes of the various methods employed; the key constituents of potential environmental significance; as well as the dominant factors governing the time-dependant leach behaviour in a typical disposal scenario. Apart from ensuring that that it is appropriate to the waste material and the required test outcomes (i.e. “fit for purpose”), the waste characterisation protocol should also allow for validation of the consistency of results between the various methodologies.

A proposed generic procedural framework for integrated and systematic waste characterisation which meets these requirements is presented in Figure 2.11.

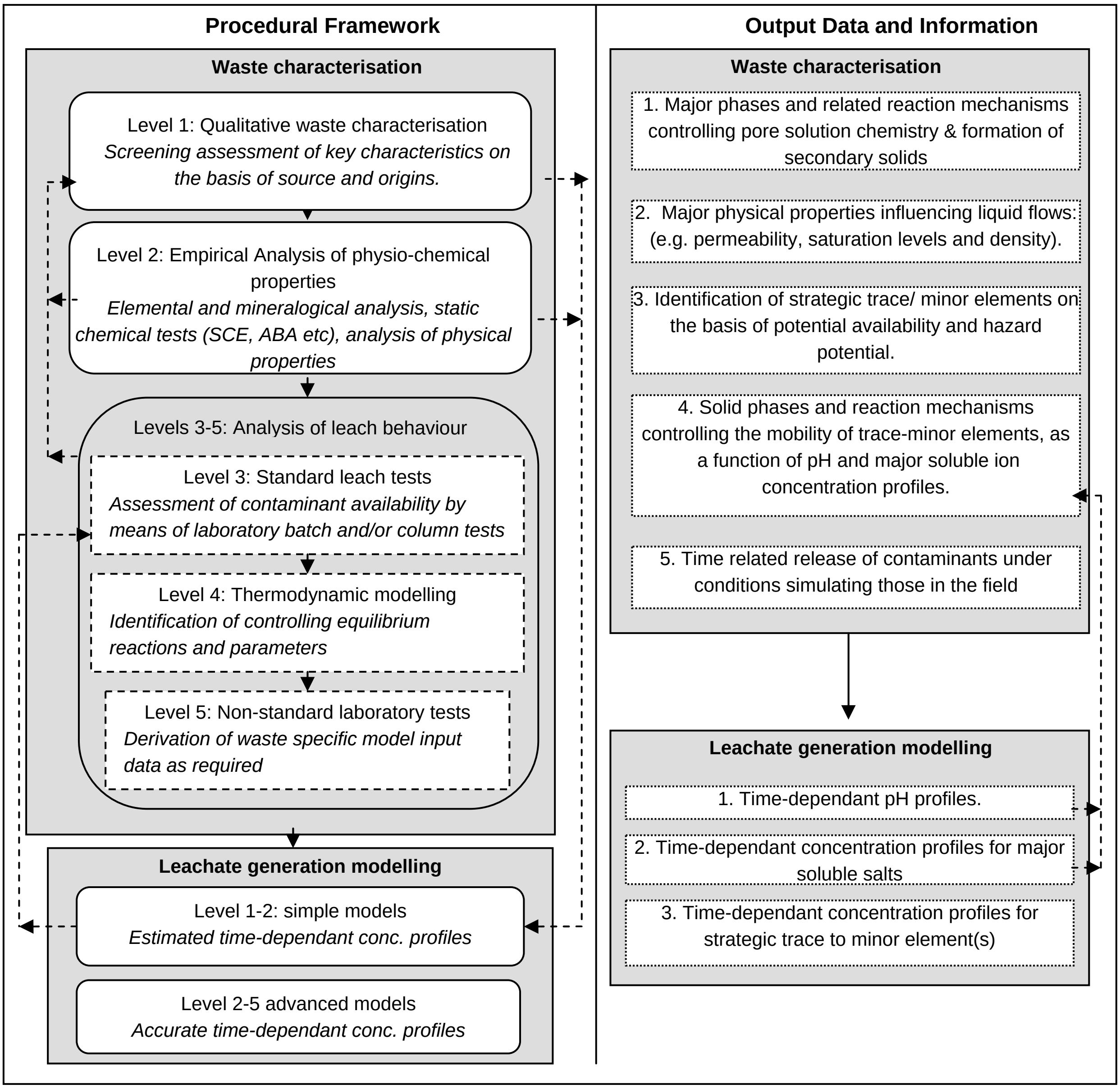


Figure 2.11: Systematic procedural framework and outcomes for waste characterisation and leachate generation predictions

In accordance with this framework, solid waste characterisation is comprised of a number of systematic and iterative stages, corresponding to various levels in terms of accuracy and detail of the derived data. Level 1 studies corresponds to the qualitative waste characterisation step described in Section 2.2, whilst levels 2-5 studies are based on empirical laboratory testwork and analysis of derived results i.e. quantitative waste characterisation. In this protocol the design of tests to investigate the leach behavior of the solid wastes (Levels 3-5) is guided and informed by qualitative waste characterisation, combined with quantitative data pertaining to the physio-chemical properties influencing potential environmental availability (Level 2). The proposed protocol also emphasises the integrated and iterative nature of waste characterisation and predictive modelling studies, as discussed within the following sub-section.

In terms of conventional laboratory-scale leach tests, the judicious manipulation of L/S ratio, pH, leach period and ionic strength in a battery of relatively inexpensive batch extraction tests, can provide information pertaining to the general types of chemical mechanisms controlling the leach reactions; the relative availabilities of the various contaminants; and the potential influence of ambient conditions for many of the reactions. Furthermore, in the case of equilibrium reactions, the controlling solids and chemical reaction equations can be derived through a fundamental thermodynamic analysis of the results from the operationally-defined availability tests. Concentration build-up tests can provide additional information pertaining to the effects of pore water compositions and ionic strengths under low L/S (<1/1) disposal regimes. Large laboratory-scale column tests are relatively expensive and time consuming, and are thus not likely to be suitable for establishing an initial understanding of, and quantitative data for describing, the leach behaviour of complex systems with a large amount of variables. The column leach protocol is, however, more representative of the flow regimes and leach behaviour in a disposal site and will thus be better suited for model validation than batch leach tests. Column leach tests can also be used to derive information and data pertaining to the hydrodynamic characteristics of the waste material, by means of tracer studies (see Petersen, 1998). Although in many cases, constants to provide the various reaction equations will be accessible in the general literature, in some instances (particularly in the case of sorption- and kinetically-controlled reactions) these may need to be derived by means of specifically designed experiments (i.e. level 5 studies in the proposed waste characterisation protocol).

2.4 Quantitative Leachate Generation Modelling: Step 4

The fourth step in the proposed impact prediction methodology involves leachate generation modelling to determine the time-dependent concentration profile of mobile constituents at the interface between the waste deposit and the surrounding environment. This is necessary as laboratory waste characterisation methods only provide a partial picture of the potential for leachate generation, and the direct extrapolation of these short-term tests results to full-scale disposal sites is generally fraught with inaccuracy and uncertainty. Subsequent interpretation of the data and information generated through systematic waste characterisation thus requires the use of mathematical formulations which model the leach behaviour of the specific waste, taking into account both the site-specific disposal scenario and waste management practices.

As inferred by the proposed protocol in Figure 2.11, the complexity of the leachate generation models, and consequently the reliability and accuracy of the generated results, will be dependent largely on how much is known regarding the mechanisms of leachate generation and how readily these mechanisms can be incorporated into a modelling structure. In some situations, such as in the case of strategic decision contexts and/or early project design stages, a simpler and/or more functional approach for the derivation of estimated leachate time-concentration profiles may be justified. Simple mathematical models based on level 1-3 estimates of contaminant availability as a function of time can be used, in conjunction with knowledge of bulk liquid flows, to derive estimates of the time-related concentration profiles in full scale deposits. Under cases of ideal plug flow, it is possible to calculate liquid flow rates as a function of waste tonnage and deposit height using simple mathematical equations based on data pertaining to rainfall ingress and the physical characteristics of the waste (solid density, saturation and porosity). Although flow conditions in actual deposits do not correspond to ideal plug flow patterns, given the inaccuracies and uncertainties associated with the estimates of time-related motilities of contaminants, particularly in the long-term, detailed hydrodynamic modelling is probably not warranted. Comparison of these concentration profiles with criteria such as water quality guidelines can subsequently be used to derive an estimate of the potential time-related environmental impact in the early project design stages. Simple models can also be used to derive an estimate of the pH and major soluble ion concentration profiles that may be expected in a full scale deposit as a result of the weathering of major phases over the long-term. This information can, in turn, be used to inform operationally-defined leach tests for the derivation of data and information pertaining to solid phases and reaction mechanism controlling the mobility of trace-minor elements (level 3 studies in the protocol represented by Figure 2.11).

Accurate and reliable quantification of the time-related concentration profiles can, however, only be undertaken through the use of a rigorous mechanistic model which takes into account both the chemical reaction and physical transport mechanisms under non-ideal flow conditions. This requires a thorough understanding of the mechanisms of leachate generation particular to the waste under consideration and relatively detailed waste characterisation (levels 1-5 in the proposed protocol presented in Figure 2.11). The complex and data intensive nature of accurate and detailed predictive models means that they are more likely to be suitable for site-specific studies, particularly in terms of optimising or improving existing operations through the application of suitable waste management and rehabilitation strategies.

Typically, rigorous mechanistic leachate generation modelling has not been attempted in impact assessment, as the processes are considered to complex. In addition, a simpler representation of a particular effect is often chosen over a more rigorous, fundamentally based approach due to limitations in data availability or computational capacity. However, with recent advances in the fields of heap leaching and waste modelling (Dixon, 2003; Gerke et al., 1998; Lefebvre at al, 2001a & b; Wunderly et al., 1996), current understanding is at the point where accurate predictive modelling is possible. Recently, Hansen (2004) developed a mechanistic generic model to specifically describe leachate generation from solid mineral waste deposits under non-ideal flow conditions, as part of her doctorial studies. The following sub-sections of the report outline the generic model structure (Section 2.4.1), as well as the proposed conceptual approach for systematically adapting this model structure to specific wastes or waste types on the basis of characterisation data and information (Section 2.4.2).

2.4.1 A generic leachate generation model structure for solid waste deposits.

The generic model structure developed by Hansen (2004) focuses primarily on the flow and transport of contaminants through solid waste deposits, so as to take into account non-ideal flow conditions in both saturated and unsaturated disposal regimes. In particular, a liquid flow structure has been developed which allows the effects of partial wetting and stagnant liquid hold-up to be investigated, both of which could be significant in waste deposit scenarios. The inclusion of partially wetted particle surface is particularly significant as it also enables the effects of direct oxygen transport to the waste particle pores in unsaturated solid deposits to be modelled.

Hansen (2004) developed the relatively sophisticated flow structure, illustrated diagrammatically in Figure 2.12, through consideration of the hydrodynamic behaviour in trickle bed reactors – which have been the topic of fairly extensive research in recent years (Iliuta et al., 1999; Kundu et al. 2001; Nigam et al., 2002). In this approach, there are three zones surrounding the porous particles, namely: a non-wetted zone; a wetted zone in contact with flowing or dynamic liquid; and a wetted zone in contact with a stagnant liquid layer. The external liquid stream is divided into an axially dispersed dynamic zone and a stagnant zone, which is adjacent to both the dynamic zone and the partially wetted porous particles. The model also incorporates external and intra-particle mass transfer resistances, the latter with the assumption that the particle micropores are completely wetted. The derivation of the model equations is detailed, together with required model parameters, in Appendix C of this report.

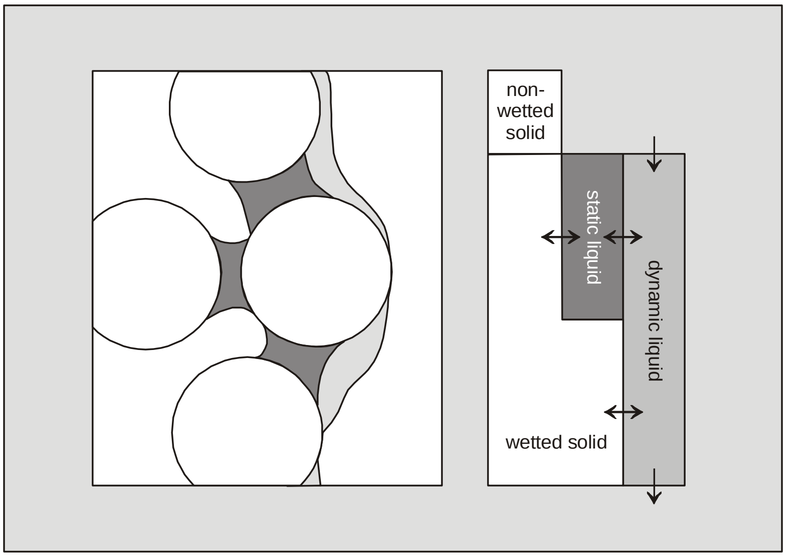


Figure 2.12: Conceptual flow structure for leachate generation modelling (adapted from Iliuta et al., 1999)

The current model is one-dimensional and does not consider transverse flow, the possibility of preferential flow paths or changing moisture contents. These assumptions are justified on the basis that the effects of these factors are not significant enough to warrant the computational effort to model them (see discussions by Hansen, 2004).

2.4.2 A conceptual methodology for waste-specific leachate generation modelling

The generic model equations outlined in the previous sub-section represent the starting point for the development of a model to describe leachate generation from specific wastes or waste types. Incorporation of the actual mechanisms controlling the release of contaminants, of relevance to that particular waste/waste type, need to be determined through waste characterisation studies (Steps 2 and 3 in the proposed methodology). Subsequent leachate generation modelling is an iterative procedure, where the conceptual model is developed based on an understanding and analysis of waste- and site-specific data and information – and revisited as new insights are gained into waste leach behaviour which validate or invalidate the assumptions made initially.

According to Zheng & Bennet (1995) the development of a proper conceptual model is one of the most important steps in a modelling study. In order to develop an accurate representation of the waste deposit it is important to avoid both oversimplification and undersimplification. An oversimplified representation of the waste deposit will fail to capture the essential features of the real-world system, resulting in a numerical model that is incapable of simulating actual leach behaviour. Then again, an undersimplified conceptual model often results in a numerical model that is too complex and too computationally demanding to be useful as an effective tool (Zheng & Bennet, 1995). In general, there is a trade-off between conceptual model complexity on one hand, and increased data requirements and computational effort on the other.

A conceptual model will always contain numerous qualitative and subjective interpretations. The appropriateness of these assumptions cannot be tested until a numerical model is developed and comparisons between simulation output and experimental or field observations are made. It should be noted that model assumptions relate not only to processes included in the conceptual model development, but also processes excluded (if they are thought to be less significant). Thus, the numerical model provides the opportunity to test and improve the conceptual model, which suggests that modelling should be an iterative procedure. This iterative procedure is depicted in Figure 2.13, which shows an algorithm for the methodology as a whole.

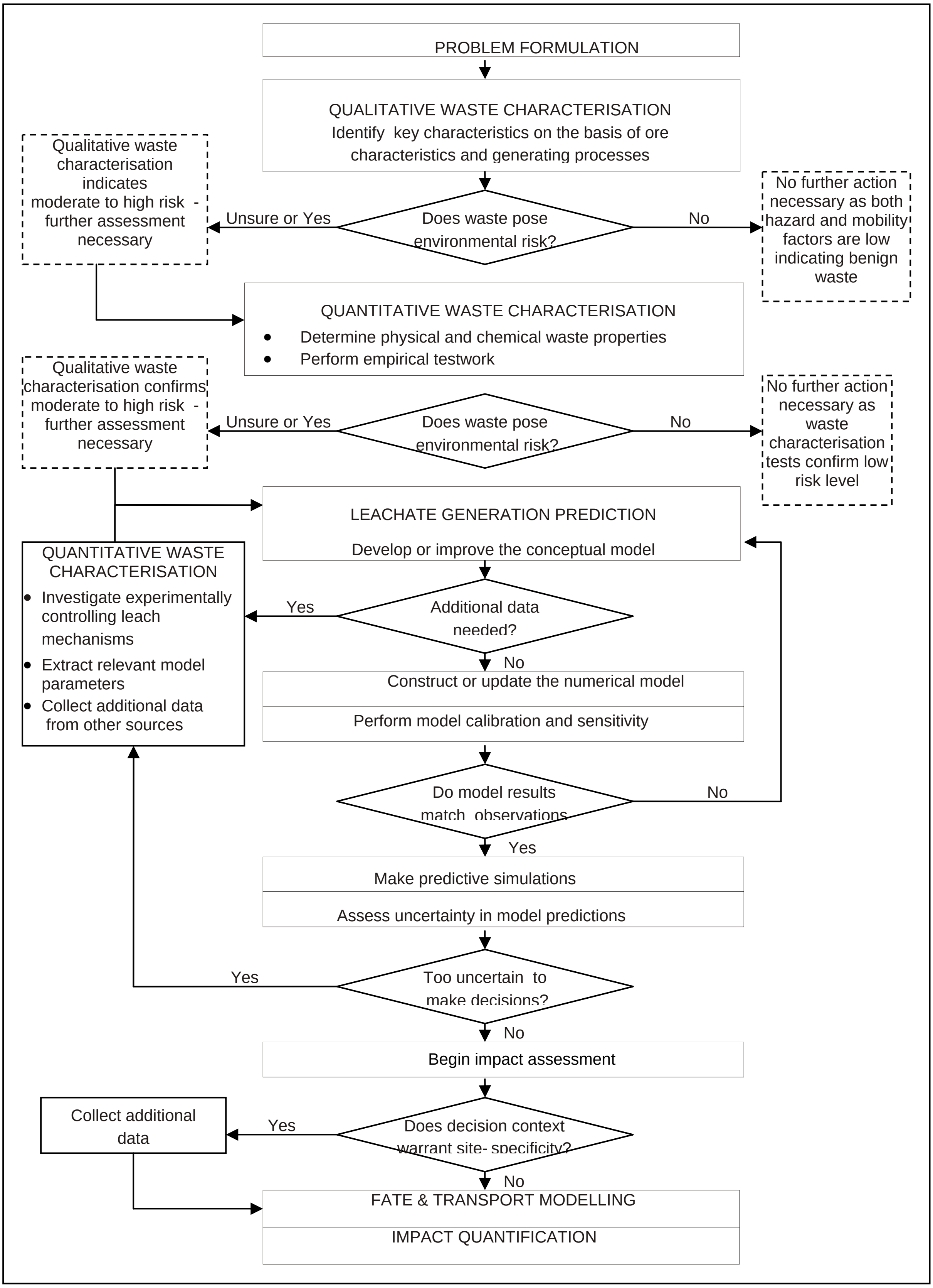


Figure 2.13: A methodology algorithm focusing on the iterative procedure required for leachate generation modelling (parts adapted from Zheng & Bennet 1995)

The numerical model also provides a guide for future data collection, particularly in those cases where additional data are needed in order to produce a conceptual model consistent with experimental observation (Zheng & Bennet, 1995).

2.5 Determining Environmental Contamination: Step 5

The fifth step of the proposed methodology involves determining the fate and transport of the leached contaminants, in order to obtain their spatial and temporal distribution within the subsurface environment. This provides a measure of the extent to which a land mass is impacted by leachate migration from the deposit. In the same way that rigorous modelling is required to quantify leachate generation, so mechanistic modelling is required here to quantify the fate of contaminants in the environment. In contrast to models for leachate generation, however, fate and transport models have been the subject of fairly extensive research and development. It is thus proposed that existing modelling tools can be used to determine the time-related environmental concentration profiles pertaining to solid mineral waste deposits.

Prior to the selection and application of an appropriate fate and transport model, it is important to first identify the more significant processes, so as to inform data and modelling requirements. To this end, an overview of the key mechanisms and parameters influencing the fate of contaminants within the subsurface environment is presented in Section 2.5.1. Existing modelling tools are subsequently reviewed and assessed in terms of their applicability for solid mineral waste leachate dispersion modelling in Section 2.5.2. Finally, a simple model case, for use in decisions where full physical and hydrogeological characterisation of the site is unavailable, is developed within Section 2.5.3

2.5.1 Contaminant plume behaviour in the subsurface environment

Leachate generated from solid mineral wastes will predominately impact the subsurface environment, contaminating soils and groundwater. Contaminants entering the subsurface environment will be diluted by transport processes and attenuated by physical, chemical and biological processes. These processes are inherently complex and the degree to which they influence contaminant movement depends on a number of inter-related factors, including both the properties of the contaminant and the site-specific environmental conditions.

According to Domenic & Schwartz (1997), mass transport processes determine the maximum extent of plume spread and the geometric character of the concentration distribution. The result of the various geochemical processes is to attenuate the spread of contaminants, reducing the size of the contaminated area to a fraction of that attributable to mass transport alone. The site-specific environmental conditions (both physical and chemical) will determine the rate and direction of mass transport as well as the rate at which geochemical reaction processes take place.

To summarise, Table 2.7 lists the relevant subsurface processes, their controlling subsurface and contaminant properties and their impact on the resulting contaminant plume. These processes are also ranked according to their relative importance in determining the fate and transport of contaminants in the subsurface.

Table 2.7: Subsurface processes – their corresponding controlling subsurface and contaminant properties and their impact on contaminant spreading (adapted from Knox et al., 1993)

Subsurface process	Subsurface property	Contaminant property	Impact on contaminant plume	Relative importance
Advection	Groundwater gradient Hydraulic conductivity Porosity	Independent of contaminant	Most important way of transporting mass away from source	✓✓✓
Dispersion	Dispersivity Pore water velocity Pore size distribution Fractures Macropores Caverns		An attenuation mechanism that reduces contaminant concentration in the plume; however, plume spreads to a greater extent than predicted by advection alone	✓✓
Diffusion		Diffusion coefficient	An attenuation mechanism of second order in most flow systems where advection and dispersion dominate	✓
Sorption	Organic content Clay content Specific surface area Cation exchange capacity Ionic strength Background ions	Valency Ionic radius Reactivity Molecular weight	An important mechanism that reduces the rate at which contaminants are apparently moving	✓✓✓
Dissolution-precipitation	pH Eh Other metals	Solubility vs. pH Speciation reactions	An important mechanism that can control the concentration of contaminant in solution; solution concentration is mainly controlled either at the source or at a reaction front	✓✓
Acid-base reactions	Subsurface minerals		Mainly an indirect control on contaminant transport by controlling the pH of groundwater	✓
Complexation	pH Ionic strength Ligand availability	Solubility vs. pH Reactivity Speciation reactions	An important mechanism resulting in increased solubility of metals in groundwater, if adsorption is not enhanced; major ion complexation will increase the quantity of a solid dissolved in solution	✓✓
Redox reactions	Eh, pH Microbial activity	Oxidation state	An extremely important family of reactions in retarding contaminant spread through the precipitation of metals	✓✓✓

2.5.2 Modelling tools for fate and transport: an overview

Groundwater flow and mass transport models have been used extensively since their development in the 1970s, and are well positioned to determine not only the spread of contaminants in the environment but also to include the important processes identified in Table 2.7 (Section 2.5.1). A number of such models have been developed which can differ quite widely in terms of objectives, mathematical approaches, processes considered, and the physical system characteristics included (see reviews by Anderson et al., 1993; Cheng & Yeh, 1998; Grove & Stollenwerk, 1987; Mangold & Tsang, 1991; van der Heijde & Elnawawy, 1993; Yeh & Tripathi, 1989). Table 2.8 summarises and describes the model types and lists some examples.

Selection of the most appropriate model will be largely based on the decision context and the associated data availability. The decisions faced by the primary industries can range from operational decisions – involving well-defined, existing systems supported by high quality site-specific data – to tactical or strategic decisions, involving hypothetical future situations and which are characterised by limited data availability. Operational decisions require prediction of future conditions and the consequences of proposed actions. Here, the selected groundwater flow and mass transport model forms an integral part of the decision-making process, and a high level of accuracy and model confidence is required. A more advanced site-specific model is therefore necessary to accurately predict environmental concentrations, and model validation is essential. For tactical and strategic decisions, the role of the selected model is to predict flow and transport in hypothetical 'generic' hydrological systems. Here, a simple model may be appropriate as the many simplifying assumptions can be justified in light of limited data availability and the required accuracy of the output.

Table 2.8: Classification of groundwater flow and mass transport models (adapted from Boulding, 1995)

Type of model	Description/uses	Examples
Flow models (porous media)		
Saturated	Simulates movement of water in saturated porous media Used primarily for analysing groundwater availability	MODFLOW
Variably saturated (vadose zone)	Simulates unsaturated flow of water in the vadose (unsaturated zone) Used in the study of soil-plant relationships, hydrologic cycle budget analysis	VS2D SWMS 2D
Mass transport models (porous media)		
Advection (particle tracking)	Particle tracking codes consider advective transport of contaminants only Useful if modelling objective is to delineate the approximate extent of capture zones or provide rough estimates of contaminant travel times	PM PATH
Dispersion	Simulates transport of conservative (non-reactive) contaminants by adding a dispersion factor into flow calculations Used for non-reactive contaminants such as chloride or as a worst-case analysis of contaminant flow	RANDOM WALK
Retardation/1st order chemical reaction	Simulates transport of contaminants that are subject to partitioning or transformation by the addition of relatively simple retardation factors or first-order rate constants to the advection-dispersion equation Used where retardation and reaction are linear and do not vary with respect to concentration Vadose zone transport models of this type use variable-saturated flow governing equations with retardation factors and first order rate constants	MT3D, MT3DMS
Geochemical reaction	Combines an advection-dispersion code with a hydrogeochemical code to simulate chemical speciation and transport Integrated codes solve all mass momentum, energy-transfer and chemical reaction equations simultaneously for each time interval Two-step codes first solve mass momentum and energy balances for each time step and then re-equilibrates the chemistry using a distribution-of-species code Used primarily for modelling behaviour of inorganic contaminants	TRANQL MINTRAN FEREACT RAFT
Hydrogeochemical models		
Distribution of species (equilibrium)	Solves a simultaneous set of equations that describe equilibrium reactions and mass balances of the dissolved elements	MINTEQA2
Reaction progress (mass transfer)	Calculates both the equilibrium distribution of species (as with equilibrium codes) and the new composition of the water as selected minerals are precipitated or dissolved	PHREEQC
Specialised models		
Fractured rock	Simulates flow of water in fractured rock Available codes cover the spectrum of advective flow, advection-dispersion, heat and chemical transport	TOUGH FRACTRAN
Heat transport	Simulates flow where density-induced and other flow variations resulting from fluid temperature differences invalidate conventional flow and chemical transport modelling Used primarily in modelling of radioactive waste and deep-well injection	
Multi-phase liquid flow	Simulates movement of immiscible fluids (water and non-aqueous phase liquids) in either the vadose or saturated zones Used primarily where contamination involves liquid hydrocarbons or solvents	
Gas flow and vapour transport	Simulates liquid/gas phase changes and movement of vapours in the vadose zone.	

Even if the decision context and associated data availability are known, model selection can still be difficult because of the many parameters and constraints to consider. Table 2.9 lists some general model selection considerations related to groundwater flow and contaminant transport parameters. Other criteria for selecting a model for fate and transport include more practical considerations such as: the availability of documentation and operation instructions; the costs associated with model purchase, set-up and training; available computer hardware and other software requirements (post-processors); usability and reliability of the code; and model quality assurance and quality control.

Table 2.9: General model selection considerations related to groundwater flow and contaminant transport parameters (adapted from Boulding, 1995)

Parameters	Selection considerations
Groundwater flow parameters	
Type of aquifer	Confined aquifers with uniform thickness are easier to model than unconfined aquifers because the transmissivity remains constant. Similarly, simulation of variable-thickness confined aquifers is more complicated than uniform confined aquifers
Matrix characteristics	Flow in porous media is much easier to model than in rocks with fractures or secondary porosity
Homogeneity and isotropy	Homogeneous and isotropic aquifers are easiest to model because their properties do not vary in any direction. If hydraulic properties and concentrations are uniform vertically, and in one of two horizontal dimensions, a 1-D simulation is possible. Horizontal variations in properties combined with uniform vertical; characteristics can be modelled in 2-D. Most natural aquifers, however, show variation in all directions and consequently require 3-D simulation, which also necessitates more extensive site characterisation data. The spatial uniformity or variability of aquifer parameters such as recharge, hydraulic conductivity, porosity, transmissivity and storativity will determine the number of dimensions to be modelled
Phases	Flow of groundwater and contaminated groundwater in which the dissolved constituents do not create a plume that differs greatly from the unpolluted aquifer in density or viscosity are easier to simulate than multiple phases.
Number of aquifers	A single aquifer is easier to simulate than multiple aquifers
Flow conditions	Steady-state flow is much easier to simulate than transient flow. Transient, or unsteady, flow occurs in the vadose zone
Contaminant transport parameters	
Concentration	The simplest way to model contaminant transport in the subsurface is to specify a starting concentration in the groundwater without considering the type of source
Type of source	For more sophisticated simulation purposes, sources can be characterised as point, line, area or volume. A point source enters the groundwater at a single point and can be simulated with either a 1-, 2- or 3-D model. Line and area sources may be simulated by either 2- or 3-D models, whereas a volume source would require a 3-D model
Type of source release	Release of an instantaneous pulse, or slug, of contaminant is easier to model than a continuous release. A continuous release may be either constant or variable
Dispersion	Accurate contaminant modelling requires incorporation of transport by dispersion. Unfortunately, the conventional convective-dispersion equation often does not accurately predict field-scale dispersion which typically requires numerical modelling of aquifer heterogeneity
Adsorption	It is easiest to simulate adsorption with a retardation factor. Non-linear adsorption and temporal and spatial variation in adsorption are more difficult to model
Chemical reaction	As with adsorption, simulation of chemical reaction is easiest when using a simple first-order rate constant. One species is easier to model than numerous interacting species. Modelling of a full suite of geochemical reactions is complicated and requires sophisticated models
Density and viscosity effects	If temperature or salinity of the contaminant plume is much different than that of the pristine aquifer, simulations must include the effects of density and viscosity variations

2.5.3 Development of a simple model case for the mineral-based resource industry

Not surprisingly, the data and information requirements for groundwater and transport modelling tend to be extensive (see Table 2.10 overleaf)

Table 2.10: Data requirements for site-specific groundwater flow modelling (adapted from Anderson & Woessner, 1992)

	Data needs
Physical framework	- Geological map and cross-sections showing the areal and vertical extent boundaries of the system (system geometry) - Topographic maps showing surface water bodies and divides - Contour maps showing the elevation of the base of the aquifers and confining beds - Isopach maps showing the thickness of stream and lake sediments
Hydrogeological framework	- Water table and potentiometric maps for all aquifers - Hydrographs of groundwater head and surface water bodies - Maps and cross-sections showing the hydraulic conductivity and or transmissivity distribution - Spatial and temporal distribution of rates of groundwater recharge - Pumping rates and artificial recharge

For most decisions faced by the primary industries, detailed site-specific modelling of the subsurface is not warranted or even practical due to limited data availability. Thus, simple models employing generic or site-generic data inputs are considered adequate for the purposes of impact assessment. Of these, the well-established groundwater flow and mass transport codes MODFLOW (McDonald & Harbaugh, 1988) and MT3D (Zheng, 1992) are considered to be particularly suitable for generating the spatial and temporal distribution of solid mineral waste contaminants in the environment. The selection of these codes is based on the criteria outlined in Table 2.9 (Section 2.5.2), supported by the fact that they are well documented, readily available, as well as widely accepted and applied in the user community. In addition, the use of the pre- and postprocessor PMWIN (Chiang & Kinzelbach, 2001) is proposed to support data entry and results extraction. PMWIN is a particularly attractive modelling tool, as proposed developments to the software – including a geochemistry add-on – will enable it to be used in site-specific as well as hypothetical generic scenarios.

The simple model case developed here makes a number of assumptions, particularly in terms of the type and number of aquifers; matrix characteristics; homogeneity and isotropy; phases and flow conditions. The modelling assumptions, consequences and potential resolutions are summarised in Appendix D of the report. It is noted that increased model complexity can be added as data becomes available or as requirements change, either through amendments to the existing model structure or employing alternative model codes. Ideally, geochemical processes should be included through an appropriate add-on in most situations due to their importance in determining the mobility and bioavailability of metals (and thus environmental impact). However, based on the number of simplifying model assumptions already present in the simple model case, the additional modelling complexity of a geochemical add-on is not warranted at this stage.

2.6 Quantifying the Environmental Impact: Step 6

The final step in the proposed methodology to assess solid mineral waste impacts is to develop an appropriate indicator or indicators to be used in environmental decision-making. Indicators are invaluable in the decision-making process as they quantify and simplify information in order to promote an understanding of environmental problems. To be useful, indicators need to be both practical and realistic – care must be taken to ensure that the indicator and the model used to obtain it are appropriate. If misleading, decisions are likely to generate poor outcomes. Pitfalls that may be experienced in choosing and using indicators according to Meadows (1998) include overaggregation; measuring what is measurable rather than what is important; dependence on a false model; overconfidence; and incompleteness.

Current indicators used to estimate ecotoxicity and human toxicity effects are over-aggregated, incomplete and dependent on models that produce unrealistic results (Hansen, 2004). While the indicators do ‘measure’ what is important (i.e. the indicators are closer to endpoints i.e. where their effects are directly interpretable in terms of human value judgements), the models used to obtain the indicators are undermined by large uncertainties and assumptions particularly those used in exposure and effects modelling.

The methodology proposed here makes use of a midpoint or proxy indicator based on the spatially- and temporally-distributed contaminated concentrations. This so-called “Impacted Land Footprint” (ILF) indicator, developed by Hansen (2004) has been adapted for use in this study, and is described in the following sub-sections of the report.

2.6.1 Deriving an appropriate decision-support indicator

The groundwater flow and mass transport models track the development of contaminant plumes from the waste deposit. The area covered by the contaminant plume is not, however, necessarily a measure of the impact. The impacted land area is only that region of the contaminant plume where the observed contamination is high enough to cause harm to some organism. To delineate the boundary between impacted land and unaffected land requires comparison of the predicted contaminant concentrations with concentration levels known to have adverse environmental effects.

Standards, such as water quality criteria, can be used to draw the boundary between acceptable and unacceptable risk to the environment as shown in Figure 2.14. Thus, even though this approach avoids exposure and effects modelling, an indication of risk is still retained. This is because standards have been developed specifically to ensure protection of the environment and are biologically and deterministically linked to endpoints. Another advantage of standards is that they are typically expressed in concentrations of particular contaminants – thus allowing direct comparison with the predicted environmental concentrations.

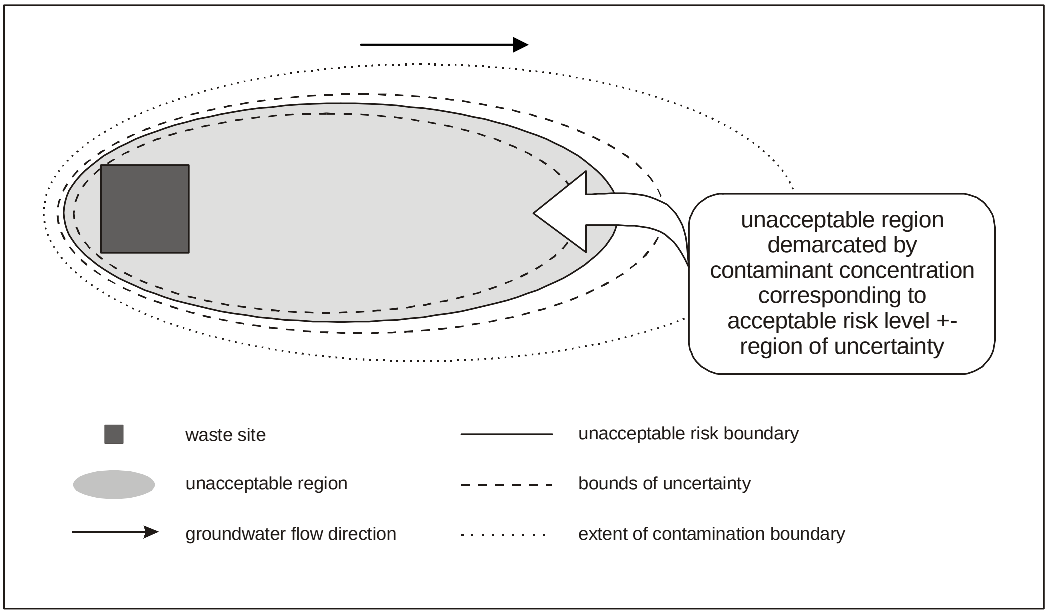


Figure 2.14: Calculation of the impacted land footprint using standards (an unacceptable region can be demarcated by the contaminant concentration corresponding to an acceptable risk level)

The impacted land footprint meets the requirements for a useful indicator as described in the introduction to this section. It makes clear the relationship between solid waste management and environmental impact. It is a tangible quantity that is easy to understand and communicate, and is thus both realistic and practical. A land footprint is also ecologically relevant.

2.6.2 Evaluating the impacted land footprint indicator

At this stage, however, the impacted land footprint is still distributed with respect to time and the number of contaminants. This represents a significant number of footprints (see Figure 2.15), which need to be condensed further into a meaningful indicator.

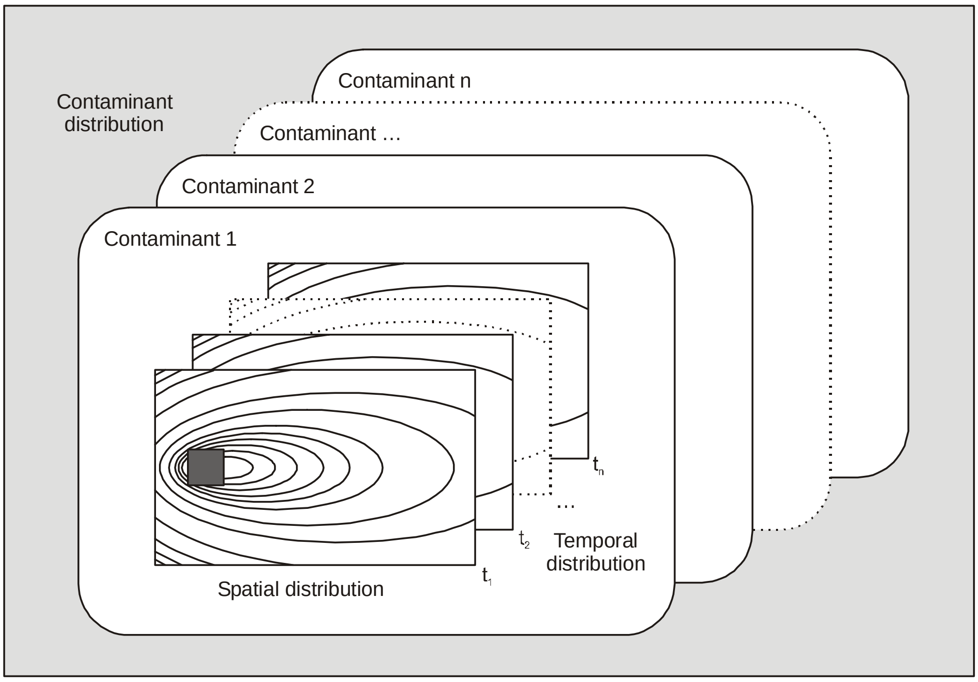


Figure 2.15: Output from groundwater flow and mass transport modelling showing spatial, temporal and contaminant distribution (Hansen, 2004)

This sub-section considers the aggregation of the impacted land footprints with respect to the number of contaminants, and proposes a method to 'capture' the time-dependent nature of the impacted land footprints in an indicator.

Aggregated impacted land footprints

The number of impacted land footprints is reduced considerably by only including those for strategic waste constituents, i.e. footprints for constituents of significance in terms of environmental impact. For the primary mineral -based industries such constituents include salts and metals.

In general, salts are seldom present in high enough concentrations to be toxic and guideline values for individual salt ions are considered unnecessary. Cumulatively, however, salts may cause significant environmental problems, and have been linked with reduced plant productivity and other physical or ecotoxic effects. An impacted land footprint based on cumulative salt concentrations is therefore a more meaningful indicator than one based on individual salt ions. Cumulative soluble salts are normally expressed in terms of salinity and are quantitatively measured as TDS (Total Dissolved Solids) or as EC (Electrical Conductivity), both of which can be relayed to ionic strength. Predicted measures of TDS, EC or ionic strength, in the contamination plume, and subsequent comparison of such with water quality guideline limits, can thus be used to define a “salinity impacted land footprint”.

An assessment of the environmental impact of solid waste disposal is not complete without a consideration of the fate of metals contained in the wastes. A trace metal footprint of impacted land is achieved using the same methods used to determine a salinity footprint – comparison of modelled output with acceptable risk levels expressed as guideline values. However, it is not practical or desirable to develop separate impacted land footprint indicators for each metal species. This is because there is significant overlap between impacted land footprints predicted for different metal species. Adding these footprints together to obtain an indicator would therefore suggest a far greater land area impacted by metals than in reality. An alternative approach is therefore required to reduce the number of metals footprints necessary to define an impacted land footprint indicator for metals. In the approach proposed by Hansen (2004), this is achieved by identifying “strategic” metals – strategic metals being those metals that are significant, both in terms of their presence in the waste and their impact on the environment. By considering only one or two metals, modelling effort is reduced considerably in both the leachate generation model and the mass transport model. An impacted land footprint indicator based on these strategic metals can be assumed to be representative of the environmental impact of all metals contained in the waste. This is because the strategic metals are selected such that their impacted land footprint can be assumed to encompass other metal footprints. Section 2.2.2 outlines a method developed by Broadhurst (2006) for identifying potentially strategic metals in solid mineral wastes, on the basis of their hazardous properties and potential availability for release to the environment in a disposal scenario.

pH is another guideline of interest in situations where leachates are characterised by extreme acidity (pH < 5.5) or alkalinity (pH> 9). In most cases, however, the main effect of pH will be indirect, and such effects will be incorporated in the determination of the salinity and metal footprints.

Capturing the time-dependent behaviour

Whilst grouping salts together as salinity and identifying strategic metals limits the number of contaminant footprints necessary to represent the environmental impact of solid waste in terms of an impacted land footprint indicator, these footprints are still distributed with respect to time. An approach is thus required to ‘capture’ the time-dependent nature of the impacted land footprints in the proposed indicator.

One such approach is the so-called “snapshot” approach, which involves obtaining the impacted land footprint at different times of interest, for example, at closure of the waste management facility or at various times post closure. Although this approach has been applied successfully in previous work (Hansen et al., 2002a & 2002b) and is relatively straightforward and computationally simple, it has the disadvantage that it does not effectively capture the time-dependent behaviour of the impacted land footprint. As indicated in Figure 2.16, it is possible to ‘miss’ the impact – and when comparing two systems it may predict results that are not a true reflection of the overall impact profiles. An alternative approach is to calculate the area under the impacted land footprint-time curve. Although integration is a common approach for condensing a time-dependent data series into a single value, such an approach will once again result in the loss of a significant amount of information regarding the time-dependent behaviour of the impacted land footprint profile. In short, both the “snapshot:” and “integral” approaches fail to capture the shape of the curve and thus the behaviour of the impacted land footprint over time.

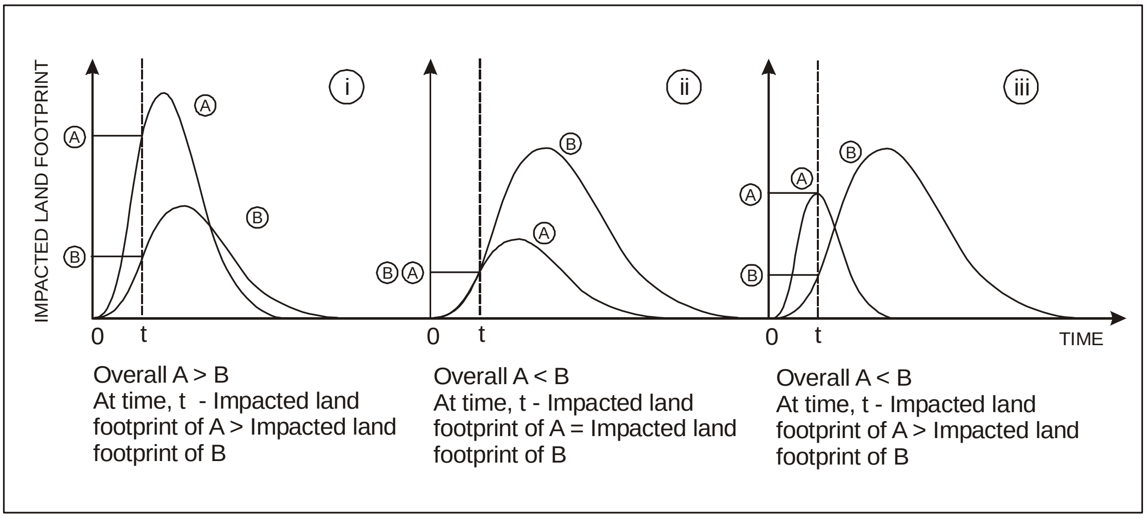


Figure 2.16: The snapshot approach for capturing the time-dependant behaviour of contaminants (where i) the snapshots at time t reflect the overall behaviour of the impacted land footprint; ii) the snapshots at time t predict an identical impact which is not the case after that time and; iii) the snapshots at time t reflect the opposite of the overall behaviour of the impacted land footprint)

Yet another approach is to develop an indicator based on parameters that characterise the shape of the footprint-time curve. As illustrated in Figure 2.17, the shape of a curve can be characterised by a number of measurable parameters. These include the maximum impacted land footprint (a measure of the physical extent of the impact in terms of land area or volume), the variance (a measure of the spread of the distribution over time) and the mean time (a measure of when the impact occurs).

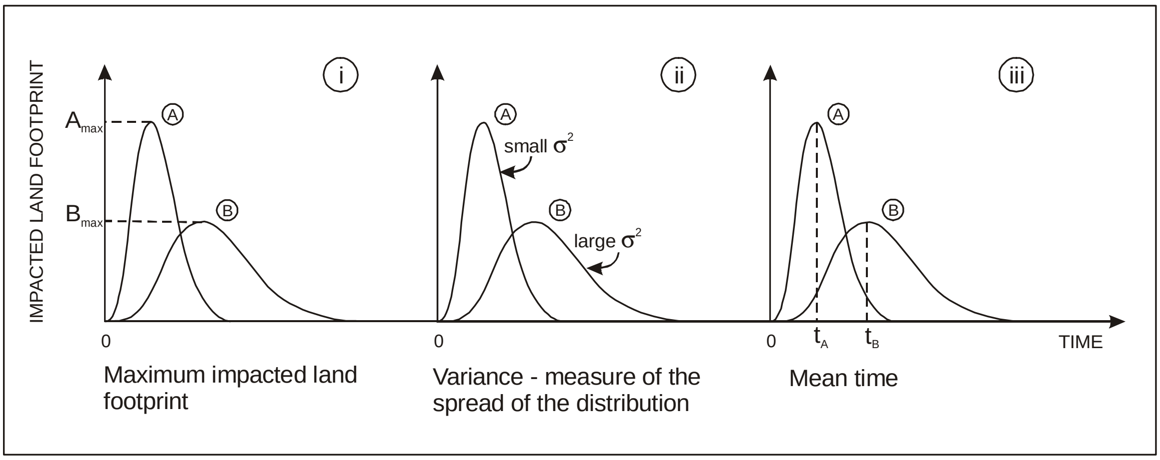


Figure 2.17: The three parameters that describe the temporal behaviour of the impacted land footprint

The impacted land footprint indicator may thus be calculated in accordance with equations 2.1 and 2.2 overleaf. Although computationally intensive, an advantage of the characteristic parameter approach, in which the impacted land footprint indicator is expressed in units of $[L^2.T^2/T]$ or $[L^3.T^2/T]$, is that each parameter may be weighted according to their perceived relative importance. For example, the land area impacted may be more important than the duration of the impact or vice versa. Similarly, a discounting can be made according to the timing of the impact based on the mean time.

Impacted land footprint indicator = $\frac{A_{max}\sigma^2}{t_A}$	Equation 2.1
variance = $\sigma^2 == \frac{\int_0^\infty (t-t_A)^2 A(t)dt}{\int_0^\infty A(t)dt} = \frac{\int_0^\infty t^2 A(t)dt}{\int_0^\infty A(t)dt} - t_A{}^2$	Equation 2.2
where, A_{max} is the maximum impacted land footprint in units of L^2 or L^3 depending on whether an impacted land area or volume is measured; σ^2 is the variance with units of $T^{2,}$ and t_A is the mean time [T].	

CHAPTER 3: DEMONSTRATION OF THE METHODOLOGY – A FOCUS ON PORPHYRY-TYPE COPPER SULPHIDE TAILINGS

In line with the second specific aim of this research project, this section of the report demonstrates application of the proposed methodology for the prediction of solid mineral waste impacts, by means of an appropriate case study. The tailings output stream arising from the early beneficiation of porphyry-type copper sulphide ore deposits has been selected for this purpose, as it is considered to be representative of many of the complexities and problems typically associated with the mineral-based resource industries. These include complex chemical compositions, large volumes and relatively high and protracted risks to the surrounding environment.

In accordance with the generic methodology outlined in the previous chapter, this case study is divided into a number of component tasks and corresponding sub-tasks, illustrated diagrammatically in Figure 3.1. Each of these methodological tasks corresponds with a separate sub-section of this chapter.

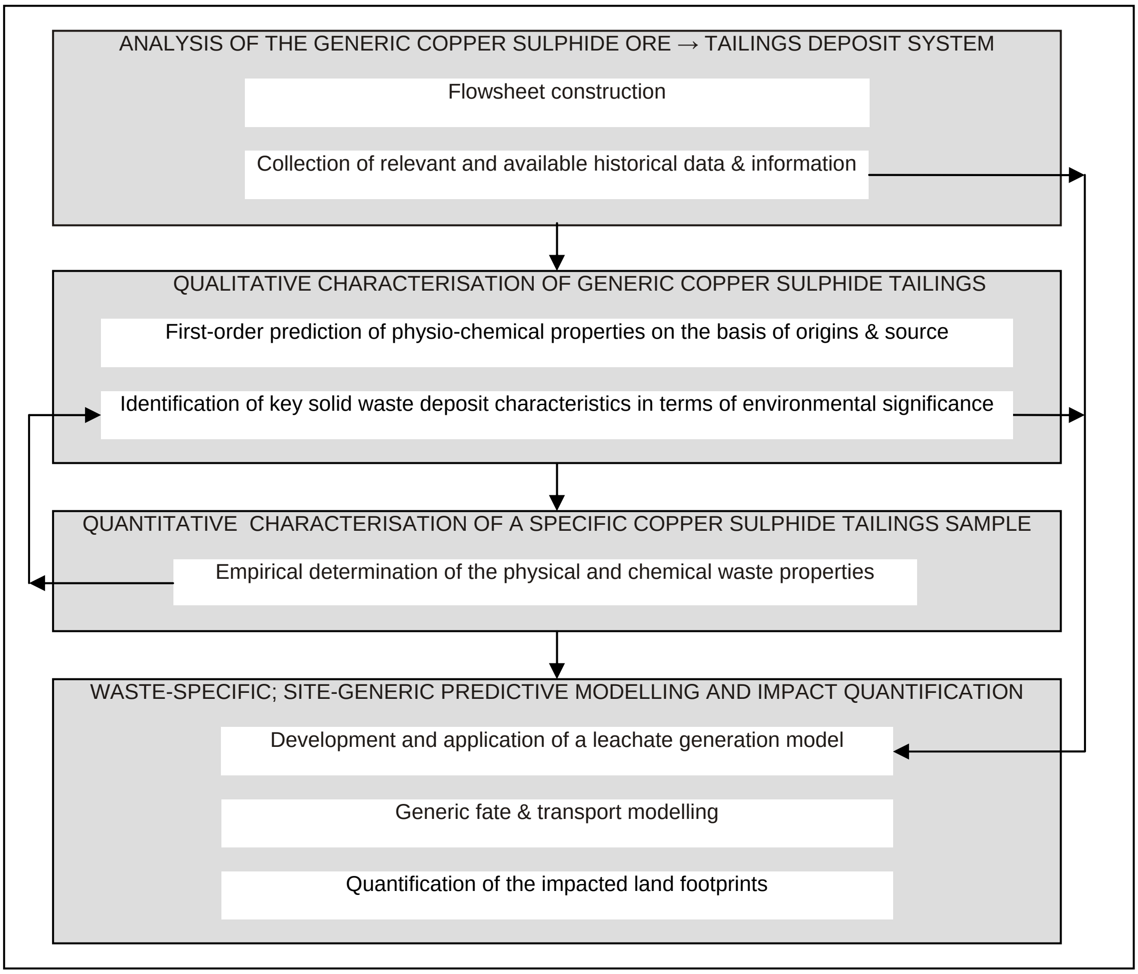


Figure 3.1: Copper sulphide tailings case study – methodological framework

3.1 Porphyry-Type Copper Sulphide Tailings: An Overview of their Generation, Management and Properties

In accordance with the discussions in Section 2.1 of the previous chapter, the identification of the system boundaries, and the collation of relevant and available data and information to describe this system, is the first task in the proposed methodology and perhaps the most important. Such information provides a detailed qualitative understanding of the system under consideration, particularly with respect to the key factors and variables influencing the performance of such; serves to make existing data more accessible and comparable; and enables current data gaps and deficiencies to be clearly identified.

This section of the report summarises and reviews the available data and general information pertaining to the generation, management and weathering behaviour of generic porphyry-type copper sulphide tailings i.e. the ore deposit → tailings deposit → leachate emissions system boundary. Specifically, Section 3.1.1 provides an overview of the genesis and chemical properties of copper sulphide ore deposits (i.e. the origins of the tailings), and the behaviour of such deposits during subsequent mining and concentration (i.e. the source of the tailings). The current data and information pertaining to the physical compositions, physical properties, management, and weathering behaviour of typical copper sulphide tailings and similar waste types is subsequently presented and assessed in Section 3.1.2.

3.1.1 The origins and source of copper sulphide tailings

Approximately 90% of the world's copper production is obtained from sulphide ores deposits, with oxidic ore deposits being relatively rare. Copper grades in sulphide deposits are relatively low, with ores from open pit and underground mines typically containing 0.5% and 1-2% copper respectively (Biswas & Davenport, 1994).

Dump and heap leaching techniques are becoming increasingly applied for the recovery of low-grade copper deposits (heap leaching) and/or previous waste rock stockpiles (dump leaching), containing copper in the range 0.15-0.25%. Higher-grade copper ores, containing on average between 0.63 and 0.65% copper, are milled and concentrated by means of froth flotation to produce a sulphide concentrate typically containing between 25 and 30 percent prior to metallurgical extraction (Ayres et al., 2002; Gordon, 2002). Although a number of hydrometallurgical processes have been developed for the treatment of copper sulphide concentrates, commercial extraction of copper from these sulphide concentrates is still almost exclusively conducted by means of pyrometallurgical techniques, with the ratio of copper sulphide concentrate feed to final copper product typically varying between 3.8 to 4/1 (Gains, 1980; Ripley et al., 1996; US EPA, 1986). A generalised flow-sheet depicting the mining and feasible process routes for the beneficiation of copper sulphide ore deposits is presented in Figure 3.2.

A number of comprehensive overviews of the primary copper industry, commercial operations and processing techniques are available in the general literature (e.g. Biswas & Davenport, 1994; Gains, 1980; Moskalyk & Alfantazi, 2003; US EPA, 1986). This sub-section is concerned mainly with the distribution, concentrations and mass flows of ore components during the mining and concentration of copper sulphide ores, containing a grade of >0.25% (i.e. ore deposit to sulphide concentrate process boundary).

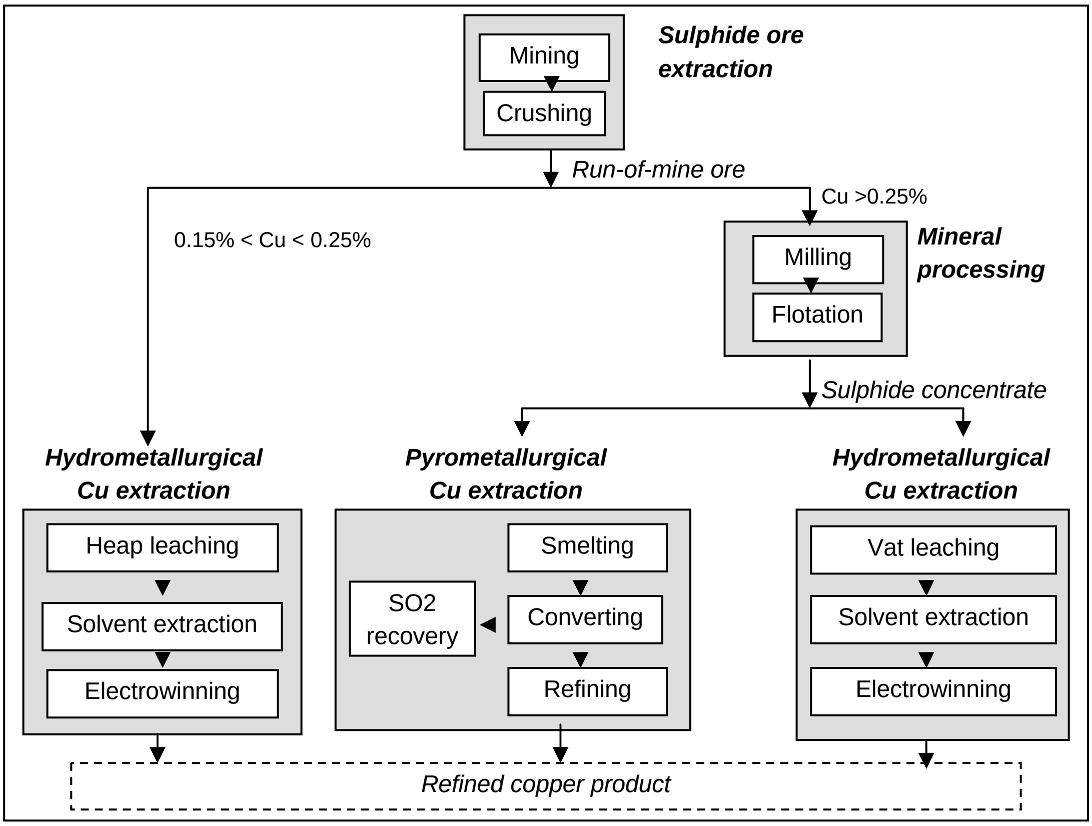


Figure 3.2: Mining and beneficiation of copper sulphide ore deposits (Biswas & Davenport, 1994)

The genesis and chemical properties of copper sulphide ores

As a general group, primary copper sulphide ore deposits are formed through the crystallisation of sulphide minerals from magmatic fluids and condensed vapours at high (hypothermal) to moderate (mesothermal) temperatures, and occur as enriched veins or massive local deposits in fissures of oxidic host rocks, comprising the major rock-forming lithophilic elements (Si, Al, Fe, Ca, K, N a, Mg).

Chalcopyrite ($CuFeS_2$) is by far the most predominant copper mineral accounting for ½ the worlds, and approximately 90% of the USA's, copper production (mining journal editorial, 1995). Other commonly occurring primary copper minerals of commercial importance include bornite (Cu_5FeS_4), and, to a lesser extent, enargite (Cu_3AsS_4), native copper, terahedrite ($(CuFe)_{12}Sb_4S_{13}$), and tennantite ($(CuFe)As_4S_{13}$). When copper materialisation is exposed in the oxidising environment at the earth's surface, copper sulphides slowly become oxidised and the released copper percolates down below the water table forming a secondary enrichment on top of the primary copper sulphide minerals. Within this layer, frequently termed a supergene zone, the grade can often be higher than the primary copper materialisation. Secondary copper sulphides such as chalcocite (Cu_2S) and covellite (CuS), and copper oxides such as cuprite (Cu_2O) and tenorite (CuO), are the most commonly occurring secondary copper minerals occurring in supergene zones. Secondary carbonates (malachite, $Cu(OH)_{2.}CuCO_3$, and azurite, $Cu(OH)_2.2CuCO_3$); hydroxy-silicates (chrysocolla, $CuSiO_3.2H_2O$) and sulphates (antlerite, $CuSO_4.2Cu(OH)_2$, brachanite $CuSO_4.3Cu(OH)_2$) also often occur with secondary sulphides and oxides in supergene zones.

Although highly enriched in copper relatively to the average crustal abundance (55 ppm), the relatively low copper grades means that copper ore deposits are a complex mixture of a number of minerals and associated elements. These deposits generally occur in association with significant quantities of iron sulphides minerals of pyrrhotite (FeS) and, in particular, pyrite (FeS_2), which are by far the most abundant and wide-spread sulphide minerals within the earth's crust. Apart from copper sulphide minerals and pyrite, a large number of minor and trace elements are also commonly associated with copper sulphide ores, the most common or well-documented ones including arsenic, bismuth, lead, zinc, selenium, tellurium, precious metals (silver, gold, PGM's), antimony, cobalt, nickel , tin, cadmium and molybdenum (Ayres, 2002; Biswas & Davenport, 1994; Ripley et al., 1996) Many of these are recovered as valuable by-products from the concentrates during subsequent beneficiation processes. In particular, the majority of the world's supply of arsenic, selenium and tellurium are almost entirely produced as by-products of the pyrometallurgical processing of copper sulphide concentrates (Ripley et al., 1996).

Copper sulphide ore deposits can occur in a variety of geological environments and are normally grouped into generic sub-classes, each defined by common geological and mineralogical characteristics such as pyrite content, host rock/gangue mineralogy and associated minor or trace minerals and metals. These sub-classes include porphyry deposits; copper skarns; polymetallic vein and replacement deposits; sedimentary deposits; massive volcanogenic deposits; and magmatic deposits, detailed descriptions of which are provided by Batty (1981); Correns (1969); Cox & Singer, (2003); Cox et al. (2003); du Bray (1996); Ďuďa & Rejl (1986); and Seal & Foley (2002) amongst others. This case study is concerned specifically with porphyry-type deposits, which are typically large, silicate-rich, carbonate-poor low-grade deposits of copper disseminated in acidic igneous rock and secondary clay minerals on the earth's surface. Copper values typically vary between 0.2-0.5%, with a high of 2%, with sulphur values varying from 0.4% to 8%. Although porphyry-type copper sulphide deposits pose a smaller environmental risk than massive copper and/or polymetallic sulphide deposits, they account for ½ the world's mine production and 93% of the US mine copper production, occurring in South America to Canada, and the pacific islands (Mining Journal editorial, 1995).

Available data and information pertaining to the chemical and mineralogical compositions of porphyry and other classes of copper sulphide ore deposits is summarised in Appendix E1

The distribution and mass flows of copper sulphide ore components during mining and concentration

The first stage in the processing of copper sulphide ore deposits comprises extraction and crushing to separate the copper-bearing ore from the host rock. The ore extraction and crushing entails the removal of large quantities of material in order to gain access to the ore, particularly in the case of open-pit mining operations commonly used to extract copper sulphide ore deposits. This material is commonly referred to as waste rock, mine waste or overburden. In reality the distinction between ore and waste rock and overburden is an economic one, with material containing less than the cut-off copper grades being considered as waste, and disposed of on waste dumps (Ayres et al., 2002). The emergence and optimisation of dump leaching techniques in recent years has resulted in profitable recovery of copper from material with grades as low as 0.15-0.2% (Ayres et al., 2002; Biswas & Davenport, 1994; Gordon, 2002). According to Ayres et al. (2002), the increased processing of material previously considered as waste rock resulted in a decrease in the ratio of waste rock to mill tailings from 3/1 in the 1970s to 1.9/1 by 2002. The copper-rich output is commonly referred to as run-of-mine or ROM ore and typically contains between 0.5 and 2% copper, with average values of 0.63-0.65% (Ayres et al., 2002; Gordon, 2002). As these grades are still too low for economic processing by smelting or vat leaching, all copper ores destined for processing by such means are first processed further to separate and concentrate the copper-bearing minerals from the gangue and non-copper bearing minerals, particularly pyrite. This is normally conducted in a two stage process comprising milling, to reduce the ore particle size to between 10µm and 100µm (Biswas & Davenport, 1994), followed by flotation to produce a copper–rich concentrate and a copper-barren waste. This waste, commonly termed flotation, mill or mineral processing tailings, accounts for the majority (>97%) of the run-of-mine (ROM) ore, with an average ratio of tailings/copper concentrate of 37/1 (Ayres et al., 2002).

The basic flow sheet for the mining and concentration of copper sulphide ore deposits is depicted in Figure 3.3.

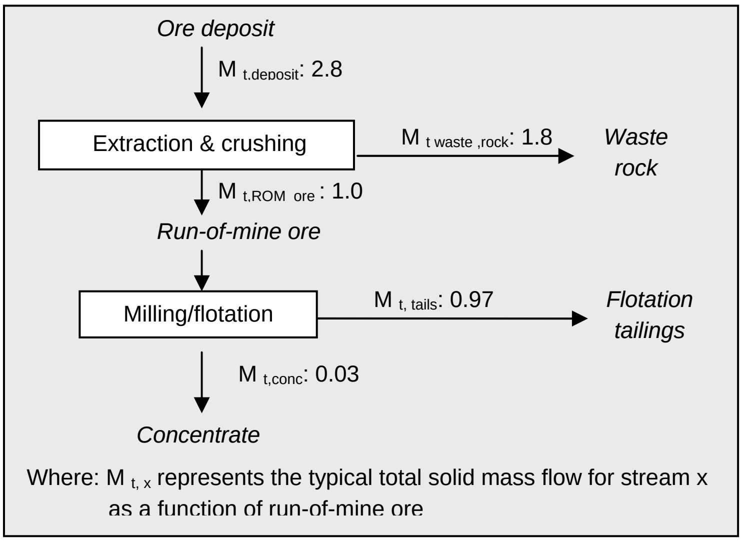


Figure 3.3: Simple flowsheet for the concentration of copper sulphide ore deposits

Apart from the majority of the gangue (>98%) and pyrite (90-95%), milling and flotation will also result in at least partial deportment of copper minerals to the tailings (10-15%), together with other trace to minor ore components (Ayres et al., 2002; Gordon, 2002). According to Ayres et al. (2002) and Gordon (2002), copper sulphide ore tailings typically contain between 0.05 and 0.15% copper. Although Ayres et al. (2002) has reported that the deportment of heavy metals during milling and flotation is similar to that of copper (10-15%), deportment values reported by other researchers (Bulatovic, 1997; Petruk & Schnarr, 1981; Wills, 1997) indicate deportment to tailings for Pb, As, Ag and Au of between 12 and 30%. Available data on the deportment of run-of-mine ore components during milling and flotation is presented in Table 3.1

Table 3.1: Distribution of sulphide ore components during milling and concentration (after Ayres et al., 2002; Benzaazoua et al., 2002; Bulatovic, 1997; Bulatovic et al. , 1998; Dreisinger, 2003; Gordon, 2002; Mwale, 2005; Petruk & Schnarr, 1981; Wills, 1997)

Ore component	Distribution (%)	
	Tailings	Concentrate
Major sulphide ore components		
Copper	5-15	85-95
Iron	77-85	15-23
Copper sulphide minerals (mainly chalcopyrite)	10	90
Iron sulphide minerals (mainly pyrite)	95	5
Minor to trace sulphide ore components		
Arsenic	25	75
Gold	12-28	72-88
Lead	21	79
Silver	25	75
Molybdenum	35-65	35-65
General heavy metals	10-15	85-90
Lithophilic gangue components	98	2
Total	95.9-99.1	0.9-4.1

3.1.2 The management and properties of generic copper sulphide tailings impoundments

The copper-depleted, fine-grained tailings slurry, generated by the milling and flotation of ROM ores, is normally discharged as waste to tailings impoundments.

This section of the report summarises the available data and information pertaining to the physio-chemical compositions; disposal methods and management; as well as the impoundment weathering behaviour of generic copper sulphide and other base-metal sulphide tailings.

Physio-chemical properties of discharge tailings slurries

Flotation of milled run-of-mine copper (and other base metal) sulphide ores, is generally carried out under alkaline conditions, with the pH typically maintained in the range 9 to 11 through the addition of lime (Wills, 1997). The tailings exit the flotation circuit in the form of a slurry, typically containing between 60% and 90% water, with a pH between 9 and 11. As expected, the tailings material is generally relatively fine, with the majority of the material occurring in the -200 to -250 µm range. Particle size distributions reported by Bulatovic (1998) and Coetzer (2003) are detailed in Appendix E3. According to values reported by Banwart & Malmstrőm (2001), Benner et al. (2000), Carlsson et al. (2002); Kontopoulos et al. (1995); McGregor & Blowes (2002); and Romano et al. (2003), absolute solid densities vary from 2.2 to 3.5 g/cm^3, with a typical value of 3 g/cm^3. Bulk densities and porosities of sulphide tailings deposits typically occur in the ranges of 1.5-1.6 g/cm^3 (Bain et al., 2000; Benner et al., 2000; Blowes et al., 1998; Kontopoulos et al., 1995; McGregor & Blowes, 2002) and 0.4-0.5 (Al et al., 2000; Al & Blowes, 2002; Bain et al., 2000; Banwart & Malmstrőm, 2001; Benner et al., 2000; Carlsson et al., 2002; McGregor & Blowes, 2002; Romano et al., 2003) respectively.

Thickening of the tailings prior to disposal is common industry practise, with the thickener overflow generally being recycled back to the mill circuit. Typical liquid/solid (L/S) mass ratio and mass water content ranges for thickened and unthickened copper (and other base metal) sulphide tailings are presented graphically in Figure 3.4.

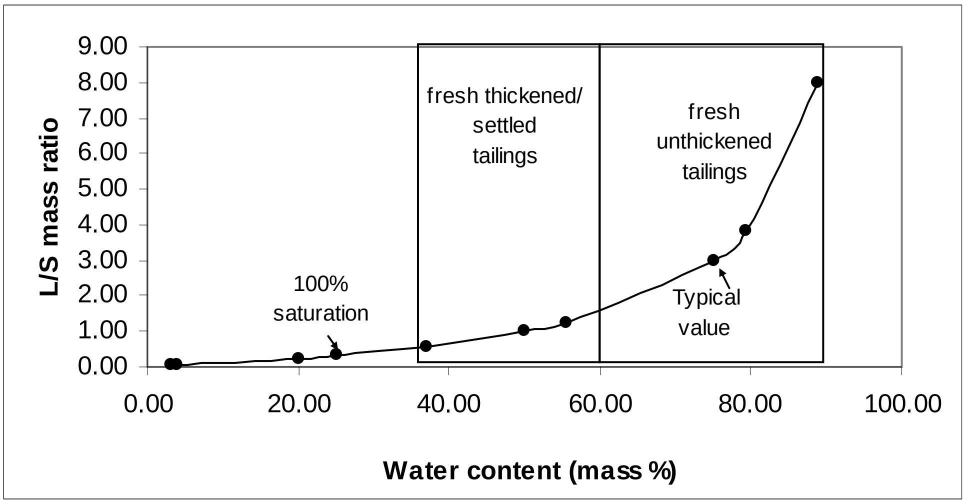


Figure 3.4: L/S mass ratios and water contents for typical tailings arising from the milling and flotation of sulphide ore deposits (based on an absolute density of 3 g/cm^3 and porosity of 0.4 to 0.5)

The values in Figure 3.4 indicate that deposits of fresh tailings will be characterised by relatively high L/S mass ratios, ranging from 1.6/1 in the case of thickened tailings to almost 11/1 in the case of unthickened tailings. Tailings corresponding to a moisture content of 75% will have an L/S mass ratio in the order of 3/1. The potential for leachate generation and hence ground water contamination in the short term due to the percolation of excess water through the deposit is thus high, and can be expected to remain so until such time as the saturation factor on the deposit approaches unity. For a typical sulphide tailings deposit this will occur at a water content of 25%, corresponding to an L/S mass ratio of approximately 0.3/1.

Available data, as compiled on the basis of a comprehensive survey of the published literature as well as discussions with certain industrial organisations, pertaining to the compositions of the solid phase of copper sulphide tailings, as well as other input-output streams in the ore-to-concentrate flowsheet are presented in Appendix E2. Sulphide tailings discharge water compositions are detailed in Appendix E3. Tailings discharge water generally has a relatively high TDS value (950-2055 ppm), which can be largely attributed to sulphate (typically between 309 and 1989 ppm) and alkalinity (1602 ppm as $CaCO_3$)

Disposal method and impoundment management

Conventionally[2], low density tailings slurry is discharged by means of spigots to specially designed impoundments formed by a containment dyke, constructed of suitable fill material or often the coarser fraction of the tailings themselves. Upon deposition, the solid fraction settles – forming a beach or delta with the water draining away to a central location or low point along the perimeter of the dam. The level of the water collected in the ponds on tailings impoundments is typically controlled through decantation by means of an embankment drain, decant towers or a floating pump. In this way seepage through the deposits is reduced, creating opportunities for optimum water usage through recycling of tailings dam return water to the processing plant.

Whilst maintaining the geotechnical stability of sulphide tailings impoundments during their operational life is paramount, it is not the only issue of concern. Discussions in the open literature (see for example Dhar, 2000; Christie, 2000; Environment Australia, 1997; ICMM, 2002; Jarvis & Younger, 2000; MMSD project, 2002) indicate that it is in fact the continued generation of acid drainage from sulphide bearing wastes that is the most serious and pervasive environmental problem related to the mining industry. Although less spectacular than catastrophic failure, acid drainage (AD) has been found to result in prolonged degradation and pollution of the surrounding environment over the long-term, with adverse consequences in terms of biodiversity conservation; quality and use of natural resources such as soil and water; as well as health and socio-economic impacts on local communities.

Historically the environmental significance of acid drainage was not fully appreciated, and historical practices based on this lack of understanding have left a legacy of abandoned and unrestored mining sites, which are the source of on-going environmental damage. Furthermore, conventional rehabilitation and remediation approaches, which deal mainly with soil erosion and dust dispersion and re-vegetation, do not address chemical stability issues adequately and there is increasing concern that they will not be sufficient to prevent post-closure impacts and guarantee a "walk-away" situation (see discussions by Jarvis & Younger, 2000; Warhurst 2000). These concerns have prompted the development of a number of methodologies for the prevention and control of acid drainage over the past decades. Approaches which are being studied or trialled (see for example Kontopoulos, 1995; Ribet et al., 1995; Romano et al. 2003; Environment Australia, 1997; MMSD, 2002) include:

- Co-disposal of tailings with acid consuming/alkali generating wastes using blending and/or layering techniques.

---

[2] Riverine and submarine disposal of tailings are also practiced at some mine sites. These practices are however highly controversial and beyond the scope of this study.

- Underground disposal
- Design and construction of liners and acid drainage collection systems
- Dewatering technologies i.e. deposition of tailings in the form of thickened sludge or paste
- Improved design and construction of engineered dry and wet covers
- Active and passive processes for the treatment of acid drainage

Source control, whereby the formation of acid drainage is avoided by preventing the sulphide minerals from coming into contact with water and oxygen, is the preferred option, and a number of covers have been designed for this purpose. Complete isolation of the tailings impoundment from the elements using covers is not however easily attained and, as pointed out by the MMSD project (2002), there are definite long-term issues with the reliability of this approach. Whilst engineered covers can be designed to minimise oxygen and water infiltrations, they are generally not able to completely prevent sulphide oxidation and acid drainage formation, and more than one approach and methodology is thus likely to be required (see discussions by Loos et al., 2000; Wates et al., 2006).

The hydrogeology and geochemistry of sulphide tailings impoundments

The chemistry of the pore water, contained in the interstitial spaces of tailings deposits, is determined by both geochemical factors, such as the rate of oxidation and metal attenuation mechanisms, as well as physical factors, such as the flow rate of water and diffusion of oxygen. These factors have been the subject of investigation by a number of authors (see for example Al & Blowes, 1999; Al et al., 2000; Bain et al., 2000; Banwart & Malmstrőm, 2001; Benner et al., 2000; Blowes et al., 1998 and 2003; Carlsson et al., 2002; Jurjovec et al., 2002; Kontopoulos et al. 1995; Lin, 1995; McGregor & Blowes, 2002; Moncur at al, 2005; Ptacek, & Blowes, 2003; Ramano et al., 2003; Ribet et al., 1995; van Huyssteen, 1998).

In accordance with the results of these studies, the weathering of sulphide tailings and generation of acid drainage commences with the oxidation of the sulphide minerals, particularly pyrite, on exposure to oxygen, and the subsequent release of soluble H^+, sulphate and Fe(II) to the tailings pore water. Whilst other less abundant sulphide minerals, such as chalcopyrite, sphalerite, galena, molybdenite and arsenopyrite, do not play as important a role in terms of the pH and ionic strength (TDS) of the pore waters, they are an important source of trace, and often highly toxic, soluble metals and metalloids. The role of oxygen in the oxidation of sulphide minerals, and hence formation of acid drainage is very significant, with the rate of sulphide oxidation being largely limited by the rate of oxygen diffusion through the impoundment. The rate and extent of oxygen diffusion is in turn highly dependant on the physical properties of the tailings, particularly moisture content and particle size distribution.

During the operational stages of a mine's life-time, tailings are normally deposited under water or maintained in a saturated condition and, due to the limited solubility (8.6 ppm at 25^oC) and diffusion coefficient (2.1E-5 m^2/s) of oxygen in water, sulphide oxidation and the potential for acid drainage generation is frequently not evident until after discharge from the mill to the tailings impoundment ceases. As tailings are generally deposited in either raised or valley impoundments, they are, however, likely to remain saturated for only a limited time after deposition has ceased. Oxidation of sulphide minerals commences as the surface of the tailings deposit becomes unsaturated and the pyrite minerals become exposed to atmospheric oxygen at the tailings surface. The oxidation rates of both the sulphide minerals and primary oxidation products (such as Fe(II) and As(III)) are furthermore frequently accelerated by various strains of bacteria. Although tailings have a relatively high specific surface area, the uniform and fine particle size leads to low permeability and reduced air and water diffusion. As a result, the ingress of rainfall is generally low (typically in the order of only 13 to 30% of the annual precipitation rate), and the tailings are characterised by a relatively slow moving water front.

Furthermore, the rate and extent of gaseous oxygen diffusion in tailings impoundments is also fairly limited, with pore gas O_2 concentrations typically decreasing from atmospheric concentrations (20.9%) at the surface of the impoundment, down to <1% in the upper few meters (Moncur et al., 2005). The reduction in gaseous oxygen concentrations corresponds to a rapid decline in the rate and extent of extent of sulphide oxidation, with active oxidation generally only occurring in the upper zones of the tailings impoundment. Although the depth of this unsaturated active oxidation zone varies according to the age of the impoundment and the management practices, a review of the literature indicates a typical depth of between 0.4 and 1.5 meters in historical tailings, with an average growth rate of 2.6 cm/year (see for example Al et al., 2000; Bain et al., 2000; Benner et al., 2000; Bezuidenhout & Rousseau, 2005; Lin, 1997; Moncur et al., 2005; Romano et al., 2003).

The production of acidic water through the oxidation of sulphide minerals in the unsaturated, active oxidation zone results in the onset of a sequence of acid neutralisation reactions. These reactions buffer the pH and deplete the primary carbonate and aluminosilicate content of the tailings, with a corresponding release of additional dissolved lithophilic constituents, principally the common rock-forming elements of Ca, Mg, Al, K, Na, Si and Mn. The products from the pH buffering reactions subsequently combine with products of sulphide oxidation to form secondary solid phases, which accumulate on grain surfaces or within void spaces among the tailings particles. The compositions and quantities of the secondary solids vary according to the depth and the age of the deposit, and are governed largely by the chemical composition of the pore water, particularly in terms of pH, redox potential and TDS (or dissolved sulphate). The spatial and time-related pore water chemistry is dependant on a number of inter-related factors, key amongst which are the initial mineral compositions of the tailings and the rate and extent of pyrite oxidation. In general, the relatively low pH and high TDS of the pore waters in the active oxidation zone coincides with the formation of iron hydroxysulphates (jarosite and schwertmannite), iron oxyhydroxides (ferrihydrite and goethite) and gypsum as the major secondary precipitates, and the pore water in this zone is generally saturated with respect to these phases. Other secondary precipitates typically occurring to a significant extent in this zone include aluminium hydroxysulphates (jurbanite and alunite) and secondary silicates (kaolinite and amorphous silica).

As the pore water infiltrates below the active oxidation zone, interaction with unoxidised tailings results in further acid neutralisation, with a corresponding increase in the pore water pH and reduction in soluble contaminants through attenuation mechanisms such as precipitation, co-precipitation and adsorption. Important precipitates include iron oxyhydroxides (ferrihydrite and goethite) and aluminium hydroxides (mainly gibbsite). Another relatively important secondary precipitate is that of covellite (CuS), which results in significant enrichment of copper in this zone in a similar manner to that which occurs in the supergene zone of chalcopyrite ore deposits. Many authors (see for example Bain et al. 2000; Dold & Fontbote, 2001; Lin, 1997; McGregor & Blowes, 2002; Moncur et al., 2005) have reported attenuation and enrichment of a number of other trace-minor metals immediately below the moving oxidation front, mainly as a result of co-precipitation, surface complexation and adsorption. As an example, McGregor & Blowes (2002) reported an increase in As (by 42-132%), Cd (by 55-99%), Co (by 52-84%), Cu (by 14-50%), Ni (38-63%) and Zn (4-145%) in this enrichment or transition zone relative to the unoxidised tailings material. Sequential chemical extraction tests to investigate the partitioning of trace to minor contaminants within the solid phases occurring below the oxidation front have indicated that a significant proportion of the enriched metals and metalloids are either weakly adsorbed or chemically bound to secondary iron precipitates (see investigations by Carlsson et al., 2002; Dold & Fontbote, 2001). Whilst the rate and extent of adsorption of metals and metalloids is dependant on a number of parameters, particularly pH, the general adsorption of heavy metals onto iron oxyhydroxides has been reported by Wilkins (2000) to decrease in the order Pb> Hg> Ag> As> Ni> Cu> Cd> Zn. These transition or enrichment zones generally occur at a depth varying between 0.5 and 3.2 m and can range in thickness from around 2-5 cm up to 15-20 cm. Apart from acting as a sink for elements solubilised during the reaction of primary components, the extensive formation of secondary precipitates below the moving oxidation front is known to cement the tailings into hardpan layers with elevated densities and depressed porosities. These hardpan layers tend to act as hydraulic and diffusive barriers towards the further migration and infiltration of water and atmospheric oxygen. Typical variations in the physical characteristics of sulphide tailings impoundments with increasing depth are illustrated in Table 3.2.

Table 3.2: Physical characteristics of sulphide tailings impoundments (ANSTO, 1999; Bain et al. 2000; Blowes at al,1998; Dold & Fontbote, 2002; McGregor & Blowes, 2002; Moncur et al., 2005)

Impoundment zone	Bulk density (g/cm^3)	Porosity	Moisture content (mass %)	Hydraulic conductivity (m/s)*
Surface	-	0.45	5 to 10	
Oxidation zone	1.43 to1.59	0.45 to 0.57	15 to 25	1.1E-6 to 9.2 E-7
Enrichment zone	1.64 to1.86	0.38 to 0.45	33	3E-8 to 4E-8
General	1.55	0.4 to 0.55	-	4.E-6 to 1.6 E-7

- Where hydraulic conductivity values are for uncovered impoundments. The use of covers typically reduces the hydraulic conductivities from average values of 1.0E-6 to 1.5E-6 m/s down to 1E-8 m/s (ANSTO, 1999).
- The oxygen flux through the tailings deposit typically varies between 2.3E-6 to 3.5E-6 mol $O_2/m^2/s$, corresponding to an effective diffusion coefficient of 2.4E-7 to 3.8E-7 m^2/s (Banwart & Malmstrőm, 2001).

Ingression of gaseous oxygen below the enrichment or transition zones is thus generally negligible (gaseous concentrations of <1%), whilst the soluble oxygen in the pore waters has been largely depleted by oxidation reactions in the upper zones. The material in this zone thus remains largely unoxidised and saturated. Further reaction of the pore water with the more reactive and soluble tailings components, such as the carbonate minerals calcite and siderite, is however expected to occur in the unoxidised zone to at least some extent, corresponding to further increases in pH and attenuation of dissolved metals and salts as the pore water migrates towards the bottom of the impoundment.

Variation in the compositions of sulphide tailings pore waters as a function of depth are summarised in Table 3.3. Detailed results are presented in Appendix E3.

An assessment of the reported compositions of the pore water in sulphide tailings impoundments as a function of depth indicates a general increase in pH and a decrease in the redox potential on going from the oxidised to the groundwater interface zone. In accordance with the conceptual acid generation-neutralisation model proposed by Morin et al. (1998), and adopted and refined by a number of other authors (see for example Bain et al., 2000; Blowes et al., 2003; Jurjovec et al., 2002), the increase in the pore water pH with depth occurs in distinct steps corresponding to the zones of precipitation/dissolution of specific solid phases, viz. ferric oxyhydroxides, aluminium hydroxides and finally carbonate minerals (siderite, followed by calcite). The pH and redox potential profiles through the tailings impoundment have important implications in terms of the concentrations of soluble contaminants. pH, in particular, is generally considered to be the master variable controlling metal mobility and speciation, both through the formation of hydroxide minerals and adsorption onto substrate surfaces. As indicated by the results in Table 3.3, the increasing and decreasing trends in the pH and redox potential respectively is generally accompanied by a reduction in the concentrations of soluble contaminants in the pore waters within the various zones. Hence whilst the concentration of soluble contaminants in the pore waters in the low pH, oxidation zone are relatively high, attenuation through secondary precipitation and adsorption results in significantly lower concentration levels in the final leachates emerging from the base of the impoundment.

Table 3.3: Summary of reported compositions of pore waters within sulphide tailings impoundments (see Appendix E3 for individual results)

	Surface zone	Oxidation zone	Transitional zone	Unoxidised zone	Groundwater interface zone
pH	3.4-3.9	2.3-4.4	5.7-6.8	4.2-7	5.7-7.8
Redox (mV)	459-621	415-621	217-359	165-354	94-456
Major soluble salts (ppm)					
TDS	3460-25000	2322-58109	14000-38120	1504-7299	665-4521
Ca	370-452	370-500	440-450	150-370	100-450
Mg	44-3000	145-2200	1780-1954	120-320	30-180
Na	20-343	12-110	70-720	8-160	8-105
K	12-40	3-70	64-86	4-67	3-22
sulphate	2410-24500	1000-50000	10000-21900	1000-5580	48-3740
Cl	16	28	54	16	5-16
Carbonate	n/a	n/a	n/a	5	54
Trace-minor chalcophilic metals and metalloids (ppm)					
Fe	19-4400	0.7-7886	254-6243	465-600	0.3-1300
Cu	0.06-2.2	0.04-2.2	0.06-0.07	0.004-0.03	0.002-0.3
Zn	80-1430	8-5000	1.3-421	4-370	0.06-42
Pb	0.008-1.1	0.007-2.5	0.007-0.3	0.2	0.0005-0.1
As	0.003-0.07	0.02-0.2	0.05	<0.02-0.1	0.002-0.02
Mo	n/a	n/a	n/a	n/a	0.0004
Cd	0.09-43	0.05-64	54	0.04-0.8	0.0004-5
Ni	0.6-20	1-8	0.7-1.1	0.06-0.2	n/a
Co	0.9-26	0.9-1.8	0.04	0.020.16	0.02
Trace-minor lithophilic metals and metalloids (ppm)					
Si	28-49	19-45	11-21	6-11	3-7
Al	34-1212	5.5-158	3.3	0.1-110	0.05-0.2
Mn	7-877	11-811	68-87	0.6-5.4	0.2-2.5
Sr	0.3	0.2	n/a	0.2	0.3
Cr	0.003-4.6	0.1-0.3	0.009	0.22	0.0006-0.01
Ba	34	44	56	237	385
V	0.09	0.02	0.02	0.02	0.02

In general the buffering capacity of the underlying tailings will limit the migration of low pH waters and harmful contaminants from the oxidation zone to the surrounding environment. The time-related pH, redox potentials and contaminant concentration profiles in the migrating pore waters will, however, be dependant on a number of inter-related factors and can vary quite significantly. A key influencing factor is the composition and mineralogy of the tailings, particularly with regards to the concentration of sulphide and acid neutralising minerals. Pore waters associated with tailings containing relatively low total sulphide mineral contents (< 20 mass % sulphide minerals), such as those arising from the processing of porphyry copper deposits, are likely to be considerably less acidic and oxidising, and have lower dissolved salt and metal concentrations, than those associated with tailings produced during flotation of massive sulphide ore deposits, which can have a sulphide mineral content of up to 60%. Typical pH and redox potential profiles for the case of tailings impoundments with sulphide contents of the same order of magnitude as those expected for the tailings arising from the milling and flotation of porphyry-type copper sulphide ore deposits (see data in Appendix E3) are presented in Table 3.4.

Table 3.4: Predicted pH and Eh profiles associated with tailings impoundments arising from porphyry-type copper deposits

	Oxidation zone	Transition zone	Unoxidised zone
pH	2.5 -4.5	4.5-5.5	5-7
Redox potential (mV)	430-650	170-340	100-320

The typical Eh-pH regions occupied by pore waters associated with porphyry-type sulphide tailings deposits are compared with the properties of both naturally occurring and contaminated water sources in Figure 3.5. The pore waters in the oxidising zone of tailings impoundments have similar Eh-pH profiles to that of mine waters, being strongly to weakly acidic and moderately oxidising. The pH profiles of the pore waters in the transitional and unoxidised zones of the tailings are, however, closer to those of naturally occurring rain water and streams, with the redox potential typically being intermediate between those of typical natural surface and groundwater sources.

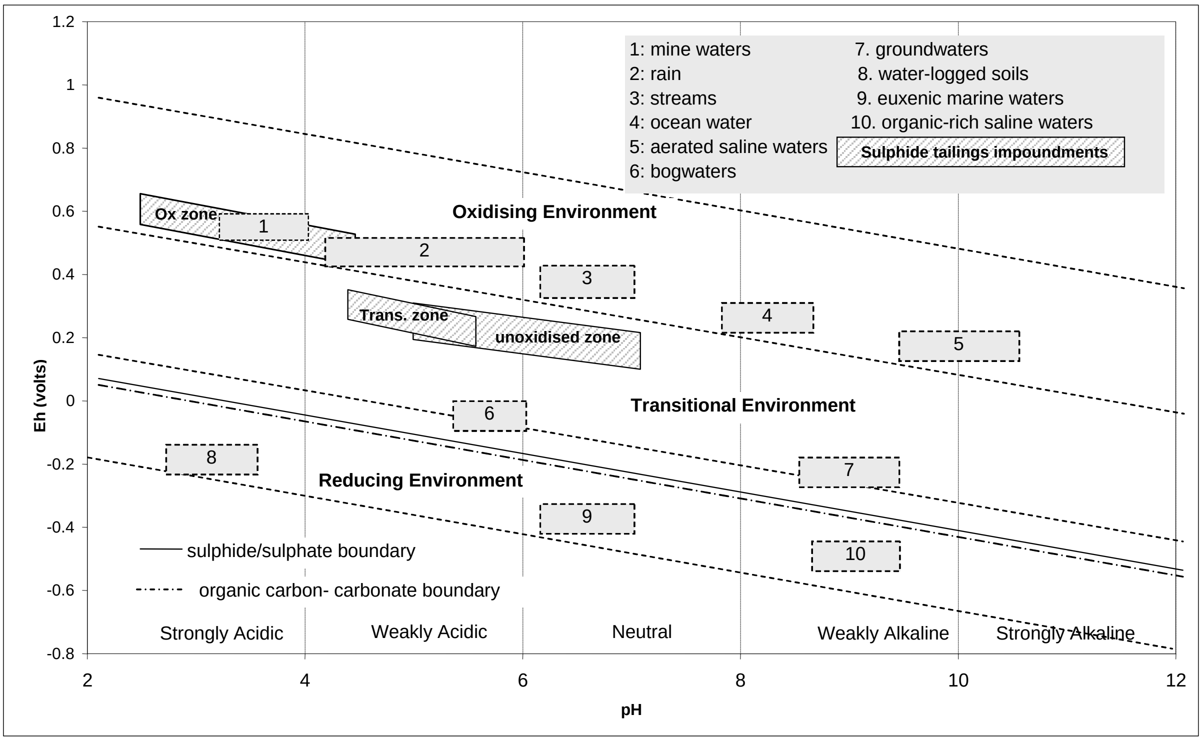


Figure 3.5: Generic Eh-pH diagram for tailings pore water and other water sources (modified from Garrels, 1960 and Brookins, 1988)

The properties of the pore waters arising from a specific tailings material will not only vary with depth (i.e. spatially), but also with time (i.e. temporally). In the early stages of weathering, dissolution of calcite can maintain the tailings pore water pH near neutral (typically 5.5-6.5), and the rate and extent of oxidation in the relatively saturated tailings is slow to negligible. As the concentrations of readily available neutralising reagents (such as calcite) become depleted and the rate and extent of sulphide oxidation near the surface of the impoundment increases, the pH of the pore water in this zone becomes increasingly acidic – with a corresponding increase in the mobilisation of metals, and dissolution of the less reactive neutralising reagents such as silicates. Mobilised contaminants which migrate from the low pH oxidation zone are largely attenuated through the formation of secondary solid phases at the higher pH values associated with the lower zones. As the sulphide content of the shallow tailings becomes depleted over time, the zone of the active sulphide mineral oxidation migrates deeper into the tailings at a rate that is dependant on the oxygen diffusion coefficient and the rate of biologically accelerated sulphide mineral oxidation. The extension of the low pH oxidation zone results in the re-mobilisation of contaminants associated with secondary solid phases, which then migrate deeper into the tailings deposit where they are re-precipitated or adsorbed. As in the case of the oxidation zone, the depths at which the secondary solid phases accumulate will become progressively lower over time. Eventually the further ingress of O_2 into the tailings and extension of the oxidation zone becomes limited by the moisture content, and the rate and extent of sulphide oxidation starts to decline as the sulphide minerals in the oxidation zone become depleted. Whilst the release of acidity may continue for some time, due to jarosite conversion and to continued advancement of low quality acidic water, a decline in the sulphide oxidation rate will be accompanied by a gradual decrease in the acidity of the pore waters and the primary release of metals to the pore water in the oxidation zone. As the tailings are exposed to fresh volumes of infiltrating water, the release and transport of dissolved metals will, however, continue mainly as a result of dissolution/precipitation and adsorption/desorption reactions of the secondary solid phases with changing pH conditions. The pH of the pore waters and the release of solid components in the transition zone are thus likely to become increasingly dominated by the compositions and chemical behaviour of the secondary precipitates over the long-term.

The time-scales of sulphide mineral oxidation and the transport of dissolved constituents can vary quite considerably. In most cases, however, the slow rate of water flow and buffering capacity of the underlying tailings or adjacent aquifer materials will limit the migration of low pH waters and harmful contaminants from the tailings impoundment to a significant extent, and environmental degradation or pollution may only occur many decades, or even centuries, after mine closure. Whilst Blowes et al. (2003) has reported peak oxidation from a tailings impoundment with a low to moderate sulphide content and a shallow water table to occur within approximately 3 decades, the migration of acidic pore waters from the Piuquenes copper tailings in Chile, which are 35 to 45 m in depth, is predicted by Wiertz (2005) to only start being evident approximately 4 centuries after mine closure.

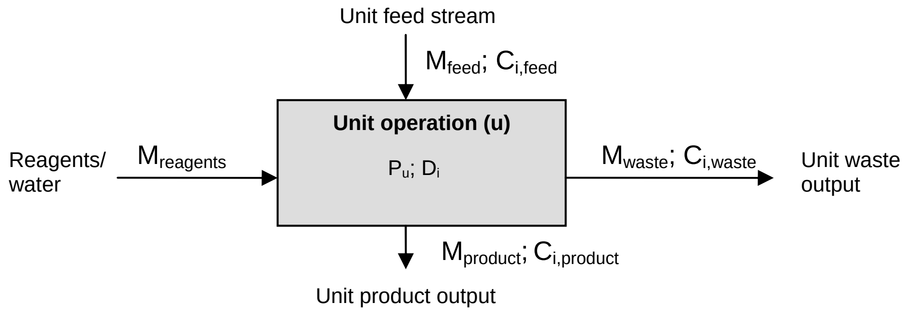
3.2 Qualitative Characterisation of Generic Porphyry-Type Copper Sulphide Tailings

In accordance with the generic methodology developed in Chapter 2 of the report, the next after problem formulation is qualitative characterisation, which is aimed at generating preliminary information on the environmentally significant characteristics of the relevant solid mineral wastestreams in a typical (or actual) disposal scenario. Such information serves to guide subsequent empirical waste characterisation and predictive modelling studies, whilst simultaneously providing decision-makers with key information in the early stages of a project life-cycle.

In accordance with the methodology developed in Section 2.2 of the report, qualitative waste characterisation is essentially carried out in two consecutive stages, namely: 1) prediction of the physio-chemical waste characteristics on the basis of their origins (ore characteristics) and source (generating processes); and 2) ranking and screening of the waste characteristics in terms of potential environmental significance.

3.2.1 Predicting physio-chemical characteristics on the basis of origins and source

The available data pertaining to input-output streams during mining and concentration of copper sulphide ores, as summarised in Appendix E2 of the report, confirms the findings of other researches (see for example Atkinson et al., 2006; Ayres et al., 2002; Stewart, 2001) i.e. that currently available data is incomplete, inconsistent and very uneven. The limitations and inconsistencies in currently available data and information pertain not only to the waste streams (waste rock and tailings), but also to the copper ore deposits from which they are generated. As ore deposits form the primary origin of all solid wastes arising from the beneficiation thereof, addressing these data gaps and inconsistencies is a prerequisite to the reliable prediction of the key characteristics of solid mineral wastes on the basis of their origins and source. An understanding of the subsequent distribution behaviour of the feed ore components, together with a knowledge of the total mass flows, during milling and flotation will enable the generation of a first-order list of potential element concentration ranges and their forms within the tailings output stream, in accordance with the relationships illustrated in Figure 3.6.



Where:

C_i: concentration of species I ; D_i: mass distribution ratio for species i relative to the feed stream mass; M_x: is the total mass flow of stream x ;$P_{u:}$ the set of operating parameters governing the unit operation

And:

$D_i = f(P_u)$; $\Sigma M_{output\ streams} = \Sigma M_{input\ streams}$; For any given species i and output stream x: $C_{i,x} = D_{i,x}.C_{i,feed}.(M_{feed}/M_x)$

Figure 3.6: Generic unit process within a flowsheet (modified from Stewart et al., 2003a)

The generic protocol for predicting chemical characteristics of ore deposits and beneficiation streams, as presented in Section 2.2 (Figure 2.5) of the report, is adapted for this particular case study in Figure 3.7.

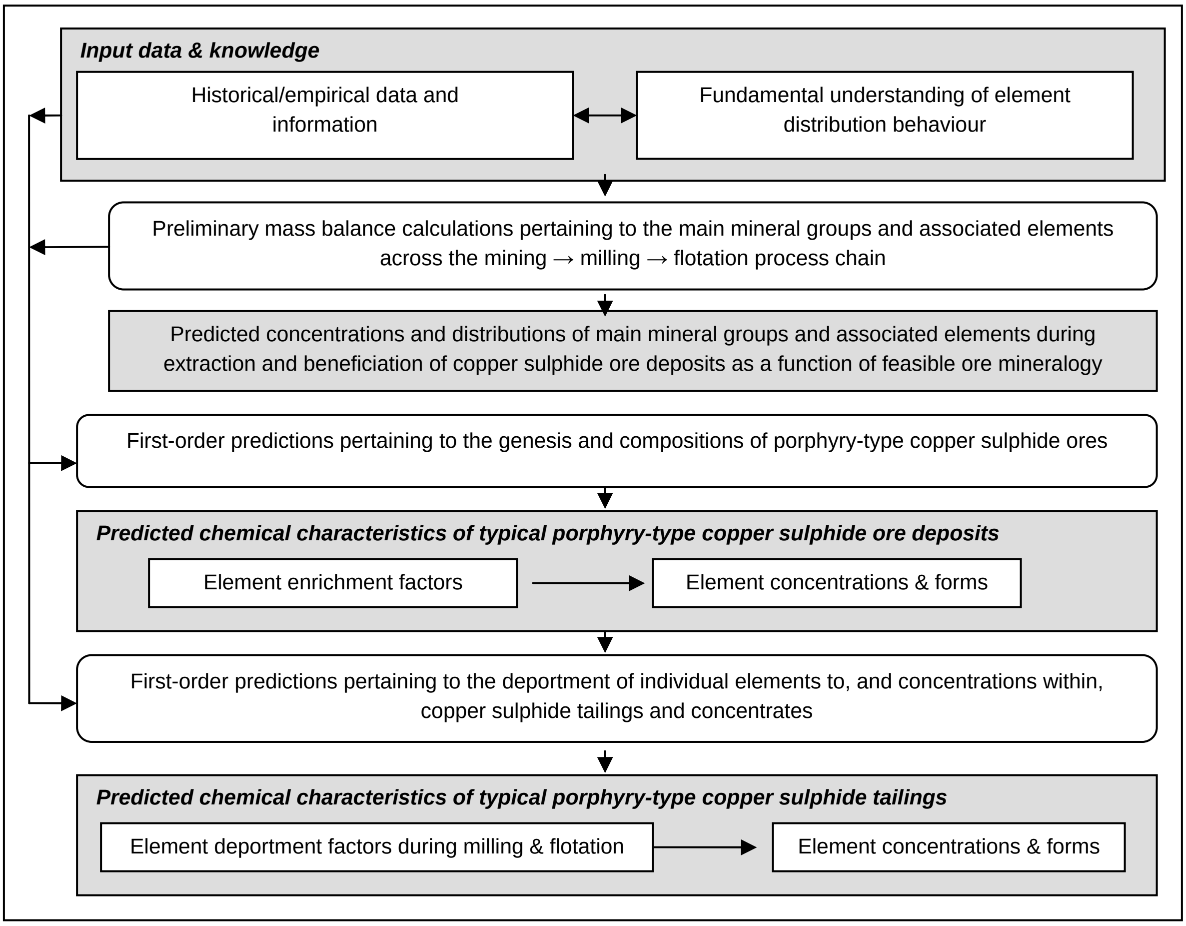


Figure 3.7: Detailed procedural framework for predicting the chemical characteristics of copper sulphide ore deposits and flotation tailings

Mass balance calculations pertaining to the concentrations, distributions and forms of major mineral groups and associated elements

A review of available data and information, pertaining to the concentrations and forms of major components in the copper sulphide ore → tailings system, indicates that the concentrate output stream is generally relatively well characterised in comparison with the other early beneficiation streams (run-of-mine ores, waste rock and tailings). In accordance with Ayres et al. (2002) and Gordon (2002), copper sulphide concentrates typically contain 23-27% Cu, 29-31% Fe and 30-32% S as the major components, and have sulphur/copper mass ratios in the order of 1.2/1. Mass balance calculations, the results of which are summarised in Table 3.5 (overleaf) indicate, however, that these "typical" major element (Cu, Fe and S) concentrations and sulphur/copper mass ratios correspond to a relatively diverse range of mineral compositions for all the relevant input-output streams. This is particularly so in the case of the pyrite/copper mineral mass ratios, with significant environmental consequences in terms of the pyrite content within the tailings output streams.

Detailed mass balance equations and assumptions are presented in Appendix F1. On the basis of these calculations, the predicted concentration ranges of the main mineral groups and their major components in porphyry-type cooper sulphide ores, tailings and concentrates are summarised Table 3.6.

Table 3.5: Predicted concentrations and distributions of major mineral groups and associated elements during mining and concentration of porphyry-type copper sulphide ore deposits

	High pyrite/chalcopyrite mass ratios				Moderate pyrite/chalcopyrite mass ratios				Low pyrite/chalcopyrite mass ratios			
	ROM ore	Conc.	Tailings	Waste rock	ROM ore	Conc.	Tailings	Waste rock	ROM ore	Conc.	Tailings	Waste rock
Concentrations (%)												
Copper sulphide minerals	1.4	46	0.08-0.2	0.1-0.2	1.9	64	0.2	0.3	2.1	72	0.2	0.3
Pyrite	9.2-18.4	35	8.5-18	1.5-3	4.0-7.9	15	3.7-7.7	0.64-1.3	2.6-5.3	10	2.4-5.1	0.43-0.90
Trace/minor ore minerals	0.3-0.8	2-8	0.02-0.09	0.01-0.05	0.3-0.8	2-8	0.02-0.09	0.01-0.05	0.3-0.8	2-8	0.02-0.09	0.01-0.05
Lithophilic gangue	80.1-91.3	11-17	81.8-91.4	96.8-98.3	90-94	13-19	92.0-95.9	98.4-99.0	93-95	10-16	94.8-97.3	98.8-99.2
Silicate gangue minerals	72-78	10-17	74-80	85-94	87-94	12-19	81-88	86-95	86-94	9-16	88-96	90-99
Carbonate gangue	≤ 9	≤1.6	≤ 9	≤10	≤ 9	≤1.9	≤ 9.2	≤ 9.7	≤ 9.6	≤1.6	≤ 9.8	≤10
Copper	0.78-0.82	26.6	0.08-0.13	0.15-0.2	0.74-0.78	25.2	0.08-0.12	0.15-0.2	0.76-0.80	26.0	0.08-0.12	0.15-0.2
Iron	4.7-9.2	27.4	4.2-8.8	0.8-1.5	2.5-4.4	28.9	1.8-3.8	0.4-0.7	1.9-3.2	30.7	1.2-2.6	0.3-0.52
Sulphur	5.6-10.8	33.0	4.8-10.2	0.9-1.7	4-5.1	31.0	3.7-4.4	0.6-0.8	2.3-3.7	31.8	1.5-3.0	0.4-0.6
Silica	25-27	3-5	26-28	27-30	25.7-40.2	3.7-5.8	26.3-41.1	27.7-43.4	16-22	2.8-3.9	16-23.5	17-24
Aluminium	8-9	1-1.7	8-9	9-10	8.3-13.2	1.2-1.9	8.5-13.5	9-14.2	5.3-9.2	0.9-1.6	5.4-9.4	5.6-9.9
Calcium	≤ 4	≤0.5	≤ 4	≤.4.4	≤ 4.2	≤ 0.6	≤ 4.2	≤ 6.5	≤3	≤ 0.5	≤ 3	≤3
Magnesium	0.6	≤ 0.1	0.6	0.7	0.6-1.0	≤ 0.1	0.6-1	0.6-1	0.3-0.6	≤ 0.1	0.3-0.6	0.-0.6
Potassium	6.5-7	0.8-1.3	6.5-7	7-7.5	7-11	1-1.6	7-11	7.5-12	4.6-7.5	0.8-1.3	4.7-7.7	4.9-8.0
Sodium	1-1.6	≤0.3	1-1.6	1.1-1.7	1.4-2	≤0.3	1.4-2.1	1.5-2.2	0.8-1.7	≤0.3	0.9-1.8	0.9-1.8
Distribution mass ratios												
Copper sulphide minerals	1	0.85-0.9	0.10-0.15	0.35-0.47	1	0.85-0.9	0.10-0.15	0.3	1	0.85-0.9	0.10-0.15	0.3
Pyrite	1	0.05-0.1	0.90-0.95	0.35-0.47	1	0.05-0.1	0.90-0.95	0.3	1	0.05-0.1	0.90-0.95	0.3
Trace/minor ore minerals	1	0.70-0.90	0.10-0.30	0.35-0.47	1	0.70-0.90	0.10-0.30	0.3	1	0.70-0.90	0.10-0.30	0.3
Lithophilic gangue	1	0.003-0.006	0.994-0.997	2-2.2	1	0.003-0.006	0.994-0.997	2-2.2	1	0.003-0.006	0.994-0.997	2-2.2
Copper	1	0.85-0.90	0.10-0.15	0.35-0.47	1	0.85-0.90	0.10-0.15	0.3	1	0.85-0.90	0.85-0.90	0.3
Iron	1	0.08-0.15	0.86-0.93	0.35-0.07	1	0.17-0.31	0.69-0.83	0.3	1	0.25-0.36	0.64-0.75	0.3
Sulphur	1	0.08-0.16	0.84-0.92	0.35-0.47	1	0.16-0.28	0.72-0.84	0.3	1	0.22-0.37	0.63-0.78	0.3
Pyrite/copper mineral ratios	7-14	0.76	62-130	7-14	2-4	0.23	19-40	2-4	1-2.5	0.14	7-15	1-2.5
Total mass ratios: concentrate/ROM ore: 0.3/1; flotation tailings/ROM ore: 0.97/1; waste rock/ROM ore: 1.8/1												

Table 3.6: Predicted concentrations of main mineral groups and their major components in porphyry-type copper sulphide ores, tailings and concentrates

Mineral group	Typical concentration (%)			Major minerals comprising each group
	Ore	Tailings	Concentrate	
Sulphide minerals Copper sulphide minerals	1.5-2.0	0.08-0.2	45-70	• Chalcopyrite: 43-97% of total • Bornite: up to 39% of total • Chalcocite: up to 17%
Iron sulphide minerals	2.5-18	2-18	10-35	Mainly pyrite
Trace to minor sulphide minerals	0.3-0.8	0.02-0.09	2-8	• Arsenopyrite: up to 10% of total • Sphalerites: up to 66% of total • Galena: typically 10% of total • Molybdenite: typically 8% of total
Total	4-20	2-18	77-82	
Lithophilic gangue Silicate gangue minerals	72-94	82-96	10-20	• Quartz: 35-45% • K-Feldspar:20- 25% • Albite:≤10% • Biotite: ≤10% • Muscovite and/or chlorite: ≤10%
Carbonate gangue minerals	0.5-7	0.5-7.5	0.1-1.5	Mainly calcite with lesser amounts of dolomite, ankerite and/or siderite
Trace to minor gangue minerals	0.5-7	0.5-7.5	0.1-1.5	• Cassiterite (SnO_2) • Iron oxides (magnetite and haematite) • Ti minerals (sphene, ilmenite and rutile) • Apatite ($Ca_5(PO_4)_3$(F, Cl. OH)) • Barite ($BaSO_4$) • Anhydrite ($CaSO_4$) • Fluorite (CaF_2) • Tourmaline ($NaFe_3Al_6(BO_3)Si_6O_{18}(OH)_4$ • Rhodocrosite ($MnCO_3$) • Zircon ($ZrSiO_4$) • REE minerals (monazite)
Total	80-95	84-98	10-20	

Predicting chemical characteristics of typical porphyry-type copper sulphide ores

Previous studies pertaining to the formation and classification of mineral deposits (see Section 2.2) have indicated that the distribution and chemical form of the elements within mineral deposits (including ores and host rocks) is controlled by their physio-chemical properties and behaviour during naturally occurring geochemical and geological activities, with certain elements having similar properties and hence exhibiting similar behavioural trends under a specific set of conditions. The studies conducted in Chapter 2 have, furthermore, indicated that the distribution and forms of elements in primary magmatic deposits such as hydrothermal copper sulphide ore deposits are mainly influenced by the relative affinities of the elements for hard “oxide-type” or soft “sulphide-type” ligands; their ionic radii relative to major rock-forming minerals; and the thermal properties of their stable forms under the high temperature reducing conditions corresponding to the formation of hydrothermal deposits in the hypo- and mesothermal temperature ranges. On the basis of this understanding, commonly occurring associations of elements and the relative extents to which such groups will be distributed to (or enriched/depleted in) typical porphyry-type copper sulphide deposits have been predicted. Reconciliation of these theoretical predictions with available data and information has given rise to the predicted enrichment factors and concentration ranges for individual elements in porphyry-type run-of-mine copper ores, as summarised in Table 3.7. Appendix F2 provides detailed calculations and element speciation information.

In accordance with this data, chalcophilic and siderophilic elements are generally enriched to a significant extent in copper sulphide ores, particularly in the case of the scarce to trace elements (Se, Te, precious metals, As, Sb, Bi, Cd, Re & Mo), all of which may be enriched in copper sulphide ore deposits to an even greater extent than copper itself. Exceptions to the rule include indium, thallium and mercury (enrichment factors < 20), the solid sulphide and elemental forms of which are considerably less stable than chalcopyrite. Furthermore, whilst the run-of mine ores will contain significant quantities of lithophilic gangue elements, the only lithophilic elements which are likely to be enriched to a relatively significant extent in hydrothermal copper sulphide deposits are those of boron, tungsten and tin, with maximum enrichment factors of up to a 100. The remaining lithophilic elements vary from being slightly depleted (enrichment factors <1) to slightly enriched (enrichment factors of 0.1-10), with the maximum enrichment factors decreasing as the average crustal abundance increases.

Predicting chemical characteristics of typical porphyry-type copper sulphide tailings

Subsequent deportment of ore components during milling and flotation will be largely dependant on their mineralogy, particularly speciation and mode of occurrence, in the sulphide ore body. Elements present as, or associated with, discrete sulphide minerals will mainly deport to the copper-rich concentrate, whilst elements present as oxides, or as inclusions in the gangue and pyrite minerals, will report mainly to the tailings. Furthermore, elements such as iron and sulphur are associated with both copper (mainly chalcopyrite) and iron (mainly pyrite) sulphide minerals, and their distributions to, and concentrations within, the output streams will be largely dependant on the ratios of the major minerals with which they are associated.

Potential element distributions during subsequent milling and flotation of the porphyry-type ROM ores have been predicted by reconciling available empirical deportment data (Table 3.1, Section 3.1.1); an understanding of the forms of the elements within typical porphyry-type copper sulphide ore deposits (see Table 3.6 and Appendix F2) and distribution behaviour of such during flotation (Section 3.1.1); and the results of the mass balance calculations pertaining to the concentrations and distributions of major mineral groups and associated elements (Table 3.5). On this basis, estimated tailings-to-ROM ore mass distribution ratios are as follows:

- Lithophilic gangue elements: 0.994-0.997
- Copper: 0.1-0.15

- Fe and S: 0.59-0.63
- Other chalcophilic and siderophilic elements: 0.1-0.3

Table 3.7: Predicted ranges for element concentrations and enrichment factors in porphyry-type run-of-mine copper sulphide ores

Element	Concentration range	Enrichment factor	Element	Concentration range	Enrichment factor
Major sulphide elements (%)			***Major lithophilic gangue elements (%)***		
Cu	0.5-1.0	100-200	Si	21-34	≤ 1.2
Fe	1-10	≤ 2	Al	4-10	≤ 1.2
S	2-11	50-200	Mg	0.2-3	≤ 1.2
			Ca	0.4-4	≤ 1.2
			K	0.3-3.4	≤ 1.2
			Na	0.3-3	≤ 1.2
Trace-minor sulphide elements (ppm)			***Trace-minor lithophilic gangue elements (ppm)***		
As	5-1800	10-1000	Ti	440-8800	≤ 2
Zn	150-1600	2-20	P	100-6000	0.1-5
Mo	15-1500	10-1000	F	60-3000	0.1-5
Pb	30-300	2-20	Mn	100-2000	≤ 2
Cd	2-200	10-1000	B	50-1000	5-100
Bi	2-200	10-1000	Ba	40-860	≤ 2
Sb	2-200	10-1000	REE	10-850	0.1-10
Ni	8-150	≤ 2	Rb	10-600	0.1-5
Se	10-100	100-1000	Sr	30-600	≤ 2
Ag	1.0-70	10-1000	Cl	10-500	0.1-5
Co	2.5-50	≤ 2	Zr	10-500	0.1-5
Ge	2-20	2-20	Li	5-300	0.1-10
Tl	0.6-6	2-10	Sn	15-300	5-100
Pt	0.05-5	10-1000	V	15-300	≤ 2
Au	0.04-4	10-1000	Cr	10-200	≤ 2
Pd	0.1-2	10-1000	Nb	2-200	0.1-10
Hg	0.2-1.5	2-20	W	5-100	5-100
Te	0.1-1	100-1000	Ga	2-80	0.1-5
In	0.1-1	2-20	Sc	1-70	0.1-5
Re	0.01-1	10-1000	Be	0.5-30	0.1-10
			Br	0.5-25	0.1-10
			Hf	0.5-25	0.1-10
			U	<1-10	0.1-5
			Ta	<1-10	0.1-10
			I	<1-5	0.1-10

Table 3.8 summarises the predicted data pertaining to enrichment factors, relative to the average crustal abundance values, and concentration ranges of individual elements in tailings derived from the milling and flotation of porphyry run-of-mine copper ores. As in the case of the feed ores, Appendix F2 provides detailed calculations and element speciation information.

As the majority of the lithophilic gangue elements deport to the tailings during subsequent beneficiation, the enrichment of elements in this stream is similar to that within the parent ore. That is, the only lithophilic elements which are consistently enriched to a relatively significant extent in copper sulphide tailings are those of boron, tungsten and tin. The predicted results also indicate that, although the deportment of trace to minor chalcophilic and siderophilic to the tailings output is only partially (< 30%), many of these elements, particularly the scare to trace elements, may still be highly enriched in the tailings relative to their average crustal abundance. This could have significant implications in terms of environmental impact (e.g. arsenic and cadmium), as well as losses in potentially valuable metal recourses (e.g. precious metals).

Table 3.8: Predicted ranges for element concentrations and enrichment factors in porphyry-type copper sulphide tailings

Element	Concentration range	Enrichment factor	Element	Concentration range	Enrichment factor
Major sulphide elements (%)			***Major lithophilic gangue elements (%)***		
Cu	0.08-0.13	15-25	Si	21-35	1-1.2
Fe	0.8-9.5	0.2-2	Al	4-10	≤ 1.2
S	1.0-11	20-200	Mg	0.2-2.6	≤ 1.2
			Ca	0.4-4.5	≤ 1.2
			K	0.3-3.5	≤ 1.2
			Na	0.3-3.2	≤ 1.2
Trace-minor sulphide elements (ppm)			***Trace-minor lithophilic gangue elements (ppm)***		
As	2-550	1-300	Ti	400-9000	0.1-2
Zn	15-500	0.2-6	P	100-6100	0.1-5
Mo	2-450	1-300	F	60-3000	0.1-5
Pb	5-100	0.2-6	Mn	100-2000	0.1-2
Cd	0.2-60	1-300	B	50-1000	5-100
Bi	0.2-60	1-300	Ba	45-880	0.1-2
Sb	0.2-62	1-300	REE	10-870	0.1-10
Ni	1-50	<1	Rb	10-600	0.1-5
Se	1-30	10-300	Sr	30-600	0.1-2
Ag	0.1-20	1-300	Cl	50-500	0.1-5
Co	0.3-15	<1	Zr	50-500	0.1-5
Ge	0.5-10	0.2-6	Li	15-300	0.5-10
Tl	0.06-2	0.2-6	Sn	15-300	5-100
Pt	0.01-2	1-300	V	15-300	0.1-2
Au	0.002-1	1-300	Cr	10-200	0.1-2
Pd	0.01-3	1-300	Nb	10-200	0.5-10
Hg	0.02-0.5	0.2-6	W	5-100	5-100
Te	0.01-0.3	10-300	Ga	2-80	0.1-5
In	0.01-0.5	0.2-6	Sc	1-70	0.1-5
Re	≤ 0.01-03	1-300	Be	1-30	0.5-10
			Br	0.5-30	0.5-10
			Hf	0.5-30	0.1-10
			U	1-10	0.1-5
			Ta	0.1-10	0.1-10
			I	0.1-5	0.1-10

3.2.2 Screening of environmentally significant tailings characteristics

As discussed in Section 2.2 of the report, the second stage of the proposed approach for the qualitative characterisation of solid mineral wastes entails the prediction of key characteristics relating to criteria of environmental significance.

In accordance with the generic methodology developed in Chapter 2 (see Figure 2.8 in Section 2.2), as well as the information gained through the review and assessment in Section 3.1.2, this will entail estimating and comparing the hazard, reactivity, attenuation, mobility and, ultimately, environmental risk potential factors for the individual elements at their maximum predicted concentration levels in a systematic and scientifically robust manner. The generic screening protocol for copper sulphide tailings constituents is summarised in Figure 3.8.

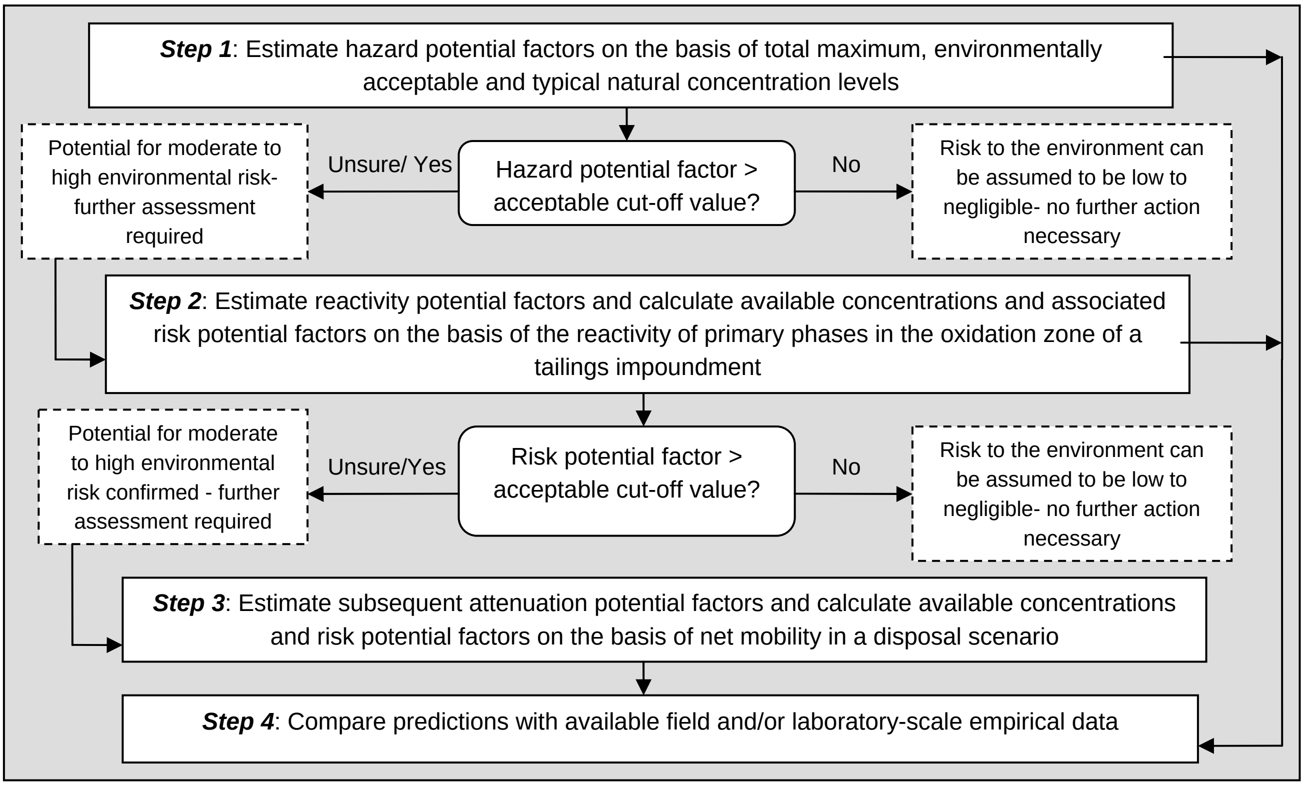


Figure 3.8: Procedural framework for the screening of potentially strategic constituents in copper sulphide tailings

Hazard potential predictions

In accordance with the proposed methodology discussed in Section 2.2 and detailed in Appendix B, a quantitative estimate of the hazard potential of the various waste constituents can be derived from their potential toxicity and human consumption effects, as well as their background concentration levels in natural environments. Furthermore, standards such as drinking water quality criteria and average crustal abundance values provide convenient surrogate measures of acceptable risk concentrations and typical natural concentrations respectively. In accordance with this, the maximum hazard potentials of elements in flotation tailings from porphyry-type copper sulphide ores have been calculated on the basis of their predicted maximum total concentrations (as derived in the previous section – see Table 3.8), typical drinking water guideline limits, and average crustal abundance values. The results of these calculations are summarised, and the elements grouped and ranked accordingly, in Table 3.9. Detailed results are presented in Appendix G1.

Assuming that solid waste constituents are only likely to pose a moderate to high risk to the environment at hazard potential factors ≥ 1000, elements in Group IV of Table 3.9 can be considered to be of low environmental significance (i.e. non-strategic). Whilst all of the elements in Groups I to III have the *potential* to be present within copper sulphide tailings at environmentally significant concentrations, only a few of elements, namely Cu, Al, Fe, Si and Cu, are likely to be present at environmentally significant levels in *all* cases.

Table 3.9: Generic ranking of potentially strategic elemental components in typical copper sulphide tailings on the basis of hazard potential

Group description	Maximum hazard potential factor/1000	Elements
I: Very high environmental significance	>10 000	As
II: High environmental significance	A: 1000-10 000 B: 100-1000	A: Cd, Mo B: **S**, Se, **Fe**, **Al**, Ag, Sb
III: Moderate environmental significance	A: 10-100 B: ≥1	A: Mn, Bi, Pb, **Si**, **Cu**, F, B B: W, REE, Sn, Cr, Ti, Be, Ni, Zn, Ca, Ba, Te, Hg, Tl, P
IV: Low environmental significance: non-strategic elements	A: 0.1-1 B: ≤ 0.1	A: K, Na, Mg, V, Zr, Re B: Cl, Sr, In, Nb, Ga, Li, Hf, Sc, Ta, Br, Au, I, Co, U, Rb, Ge

Calculations:

Hazard potential factor = (*m*.*n*)(solid concentration(ppm))^2 /[(*m*.water quality criteria (ppm)). (*n*.average crustal abundance (ppm))] (see Appendix B for detailed explanation of the ranking methodology)

Assumptions:

- the effect and enrichment are of equal importance: i.e. the weighting factors *m* and *n* are both equal to 1
- solid waste constituents are likely to pose a moderate to high risk to the environment at hazard potential factors ≥ 1000
- elements in bold are likely to be of environmental significance even at the minimum predicted concentration levels (see Table 3.8 and detailed results in Appendix G1)

Reactivity and associated risk potential predictions

As discussed in Section 2.2 of the report, a measure of the potential risk posed by a particular waste constituent needs to be based not only its inherent capacity to cause harm or damage (i.e. on its hazard potential), but also on its potential to be available for release to the environment (i.e. its availability potential).

In accordance with the proposed procedural framework in Figure 3.9, the fraction of a solid waste which is potentially available for release from a solid waste under disposal conditions will be dictated in the fist instance by the extent of weathering and alteration of the primary mineral phases under disposal conditions. This, in turn, will be governed largely by the oxidative dissolution of sulphide minerals within the oxidation zone, and acid hydrolysis of primary carbonate and silicate minerals in the oxidative and transitional zones of the impoundment, both of which are governed by slow, kinetically-controlled reaction mechanisms.

Table 3.10 summarises the predicted reactivity potential reactivity factors for the various primary mineral phases as derived through consideration of:

1. General literature information (Ďuďa & Rejl, 1986; Thornton, 1983) and published pH-potential diagrams (Brookins, 1988; Garrels, 1960) pertaining to the potential thermodynamic stability of the primary mineral phases under the likely Eh-pH conditions associated with the oxidation and transitional zones of a typical tailings impoundment (described in Table 3.4, Section 3.1).
2. The results of empirical sequential chemical extraction (SCE) studies conducted by Carlsson et al. (2002) and Dold & Fontbote (2001) on material from the unoxidised zone of base metal sulphide tailings impoundments.

The available qualitative thermodynamic stability information and empirical SCE data is summarised in Appendix G2.

Table 3.10: Predicted reactivities of the constituents associated with primary phases within the oxidation and transitional zone of typical copper sulphide tailings impoundments

Thermodynamic stability	Predicted reactivity potential factors	Associated elements
Unstable	0.9-0.95	Chalcophilic elements present almost exclusively as primary sulphides: As, Cu, Pb, Se, Cd, Mo, Sb, Te, Ag, Bi, Zn, Ge, Hg
Partially stable	A: 0.75-0.95	A: Elements present largely as unstable sulphide or carbonate minerals but partially as stable gangue minerals: Mn and Fe
	B: 0.5-0.8	B: Elements present to a significant extent in both stable and unstable forms: Ca and Mg
	C: 0.4-0.6	C: Elements present as partially stable oxides: W, F, P, U
Stable	0.1-0.3	Elements present as acid insoluble silicates and oxides: Al, K, Na, Ba, Ti, V, Cr, Cl, Be, Li, Rb, Sc, REE, Sn, Ga, B
Inert	0-0.05	Elements present as stable metals and oxides: Si, Zr, Hf, Ta, Nb, Au

Risk potential factors, derived through the substitution of the total concentration for each element with that fraction likely to be mobilised within the oxidation and transitional zones of the impoundment through primary dissolution reactions, are presented in Table 3.11. Detailed results are presented in Appendix G1.

The results indicate that many of the lithophilic gangue elements identified as having a moderate hazard potential (Si, Ca, Ba, Be, REE, Cr, P, Ti and Sn) are present within the tailings as relatively stable oxides and/or silicates and will thus not pose a significant risk to the environment in a disposal scenario. Similarly, on the basis of the stability of the primary Al-K-silicates within a typical tailings impoundment, aluminium is only predicted to pose a moderate risk to the environment, in comparison to its relatively high hazard potential.

Prediction of attenuation and availability potential factors for selected metals

The fraction of solid waste which is potentially available for release from a solid waste also needs to take account of the extent to which potentially significant elements, mobilised through weathering of the primary phases, are likely to be attenuated through secondary precipitation and/or adsorption reactions. Together, the reactivity and attenuation potential factors enable calculation of the net availability potential factor, i.e. the net mass fraction of element in the solids predicted to be available for release to the environment over the expected deposit life time (which is typically 100 to 500 years, Hansen (2004)).

Table 3.11: Generic ranking of potentially strategic elements in typical copper sulphide tailings based on predicted maximum reactivities of primary solid phases in the oxidation and transitional zones

Group description	Maximum risk potential factor/1000	Elements
I: Very high environmental significance	>10 000	As
II: High environmental significance	A: 1000-10 000	A: Cd, Mo
	B: 100-1000	B: **Fe**, **S**, Ag, Se, Sb
III: Moderate environmental significance	A: 10-100	A: Mn, Bi, **Al, Cu**, Pb
	B: >1	B: Ni, Te, Hg, F, B, Zn, W
IV: Low environmental significance: non-strategic elements	A: 0.1-1	A: REE, Si, Tl, Sn,Ca, Ti, Be,Mg, P, Ba
	B: ≤ 0.1	B: K, Re, In, U, Na, V, Rb, Cl, Sr, Ga, Li, Zr, Sc, Br, Nb, I, Hf, Ta, Au, Cr, Ge, Co

Calculations:

- Reactive concentrations (ppm) = reactivity potential factor x total element concentration in solid tailings (ppm)
- Risk potential factor = (*m*.*n*)(reactive solid concentration(ppm))^2 /[(*m*.water quality criteria (ppm)).(*n*.average crustal abundance (ppm))]

Assumptions:

- the effect and enrichment factors are of equal importance: i.e. *m*=*n*=1
- solid waste constituents are likely to pose a moderate to high risk to the environment at risk potential factors ≥ 1000
- elements in bold are likely to be of environmental significance even at the minimum predicted concentration levels (see Table 3.8 and detailed results in Appendix G1)

In accordance with the review and assessment in Section 3.1, precipitation, co-precipitation and adsorption reactions are important controls on the concentrations of waste constituents in the tailings pore waters, particularly over the long-term. The surfaces of ferrihydrite, also referred to as hydrous ferric oxide (HFO), are particularly important sites for retention of metals and metalloids, and are dominant secondary solid phases in tailings impoundments. In contrast to the oxidative dissolution and acid hydrolysis reactions described above, the solid phase precipitation and adsorption reactions are generally rapid, equilibrium-controlled reactions. This suggests a role for predictive thermodynamic models (also termed equilibrium speciation modelling or aqueous geochemical models), which can predict the extent of constituent attenuation through precipitation and adsorption reactions in response to changing redox potential, pH and solution composition. A particular advantage of thermodynamic models in predicting the extent of mobilisation of solid waste constituents in a disposal scenario is that they provide data on the concentrations *as well as the speciation* of elements in the leachate and the likely controlling reaction mechanisms. Two commercially available thermodynamic models have been used to identify the key attenuation mechanisms and to estimate the extents of attenuation of selected sulphide tailings constituents (specifically those elements in groups I-III of Table 3.11), viz: Visual MINTEQA2 version 4.0 of the US EPA CREAM (upgraded in April, 2005) and Outokumpu HSC Chemistry® for Windows, version 5.1 (upgraded in October 2002). A detailed example to illustrate how these two thermodynamic models are combined with published thermodynamic data for the determination of iron attenuation (through secondary precipitate formation) and speciation is provided in Appendix G3.

Attenuation and availability potential factors for, as well as the key reaction mechanisms governing, selected elements on the basis of the thermodynamic modelling outcomes, are presented in Table 3.12.

Table 3.12: Attenuation and net availability of selected elements in typical copper sulphide tailings impoundments: First-order predictions

Element	Dominant attenuation mechanism(s)	Attenuation potential factor	Availability potential factor
Extensive attenuation			
Arsenic	Adsorption onto hydrated ferric oxides	0.98-1.00	<0.02
Lead	• Precipitation of anglesite ($PbSO_4$) and/or • Adsorption by ferrihydrite	0.99-1.00	<0.01
Selenium	Precipitation of copper selenides (Cu_2Se).	0.95-1.00	<0.05
Molybdenum	• Precipitation of calcium molybdate ($CaMO_4$) and/or • Adsorption by ferrihydrite	0.98-1.00	<0.02
Antimony	Precipitation of oxides $Sb(OH)_3$ and/or Sb_2O_4	0.97-1.00	<0.03
Iron	Precipitation of jarosite, ferrihydrite, goethite and, to a lesser extent, schwertmannite	0.97-1.00	<0.03
Tellurium	Precipitation of Cu_2Te and/or TeO	0.99-1.00	<0.01
Silver	Formation of metallic Ag	>0.99	<0.01
Bismuth	Precipitation of Bi_2O_3	0.98-1.00	<0.02
Aluminium	Precipitation of alunite, gibbsite and, to lesser extent , jurbanite and kaolinite	0.99-1.00	<0.003
Copper	• Metallic copper formation and, to a lesser extent, chalcocite (Cu_2S) • Adsorption by ferrihydrite	0.9-1.0	<0.1
Mercury	Metallic Hg	>0.99	<0.01
Barium	Precipitation of barite ($BaSO_4$)	>0.99	<0.01
Platinum	Formation of metallic Pt	>0.99	<0.01
Tungsten	• Precipitation of $CaWO_4$ • Adsorption by ferrihydrite	>0.98	<0.02
Partial attenuation			
Cadmium	• Adsorption by ferrihydrite. • Partial precipitation of $CdCO_3$ possible at pH ≥ 6.	0.35-0.85	0.15-0.60
Zinc	• Adsorption by ferrihydrite • Partial precipitation of $ZnCO_3$ possible at pH ≥ 6.5	0.20-0.50	0.45-0.75
Nickel	Adsorption by ferrihydrite	0.25-0.85	0.15-0.70
Calcium	Precipitation of gypsum ($CaSO_4.2H_2O$)	0-0.40	0.30-0.80
K and Na	Precipitation of jarosites	0-1.00	0-0.30

Table 3.12 continued…..

Element	Dominant attenuation mechanism(s)	Attenuation potential factor	Availability potential factor
Low attenuation			
Manganese	• Adsorption by ferrihydrite. • Partial precipitation of $MnCO_3$ possible at $pH \geq 6$.	<0.25	0.60-0.95
Sulphur	• Precipitation of gypsum and hydroxy sulphates of Fe and Al • Partial adsorption by ferrihydrite possible	<0.20	>0.70
Germanium	Precipitation of GeO_2	<0.01	>0.90
Boron	Adsorption by ferrihydrite	<0.07	0.10-0.30
Magnesium	Adsorption by ferrihydrite	<0.05	0.45-0.80

Calculations:

Attenuation potential factor = [(% precipitation) + (% adsorption)]/100

Availability potential factor = reactivity potential factor x (1-attenuation potential factor)

Calculations based on:

- Predicted reactivity potential factors as presented in Table 3.10
- Pore water compositions and Eh-pH ranges as presented in Appendix G3
- Ferrihydrite surface complexation equilibrium constants as provided by the Visual MINTEQA2 ver. 4.0 surface complexation data base (“feo-dlm.mdb”)
- Assumed ferrihydrite solid concentrations of 10 g/l in the lower pH (4.5-5.5) zones, and 1g/l in the deeper, higher pH (6-7) zones.

Risk Potential Factors

In accordance with the generic methodology outlined in Section 2.2 (Chapter 2) and detailed in Appendix B, the final risk potential factors for selected constituents can be derived by substituting the total element concentration with the available element concentration, as determined from the predicted availability potential factors (Table 3.12). Maximum risk potential factors, derived on this basis, are summarised, and selected elements grouped and ranked accordingly, in Table 3.13. Detailed results are presented in Appendix G1.

The risk potential factors and hence relative environmental significance of the waste constituents will be highly dependant on their total concentrations in the tailings, which in turn will be dependant to a greater extent on their concentrations within the feed ore. Hence, whilst all of the elements in Groups I to IV (particularly Cd and, to a lesser extent, As, B, Mo and Se), have the *potential* to be present within copper sulphide tailings at environmentally significant concentrations, only S and Mn are predicted to be consistently present at environmentally significant levels (see Table 3.13 overleaf)

Table 3.13: Generic ranking of selected elements in typical copper sulphide tailings on the basis of predicted maximum available concentrations under typical disposal conditions

Group description	Maximum risk potential factor/1000	Elements
I: Very high environmental significance	>10 000	None
II: High environmental significance	A: 1000-10 000 B: 100-1000 C: 10-100	A: Cd B: S* C: Mn*
III: Moderate environmental significance	1-10	As>B, Mo, Se
IV: Low environmental significance	0.1-1	Sb, Zn, Ni, Fe, Si, Ca, Cu, Mg, F
V: Non-strategic elements	≤ 0.1	Bi, Na, Al, Ag, Ba, W, Te, Pb, K, Ge, Hg, REE

* elements in bold are likely to be of environmental significance even at the minimum predicted concentration levels (see Table 3.8 and detailed results in Appendix G1)

Calculations:

Available concentration = availability potential factor x total solid concentration

Risk potential factor = ($m.n$)(available solid concentration)^2 /((m.environmentally acceptable concentration).(n.typical natural concentration))

Assumptions:

- the effect and enrichment factors are of equal importance: i.e. $m=n=1$
- solid waste constituents are likely to pose a moderate to high risk to the environment at risk potential factors ≥ 1000

Reconciliation of predicted and available data

Available data pertaining to the compositions of pore waters from actual sulphide tailings impoundments, as summarised in Table 3.3 in Section 3.1, is reconciled with typical drinking water quality guideline limits in Table 3.14 (A and B).

A comparison of the empirical data in Table 3.14 with the predictions reported in Table 3.13 confirms that there is a high probability that both manganese and sulphate will be present in migrating tailings pore waters at concentration levels which will have a significant impact on the surrounding environment. The field results also confirm that, depending on their initial solid concentrations, arsenic and zinc may also be of direct environmental significance. Discrepancies, however, exist with regards to cadmium, iron and the major soluble cations, particularly calcium. Whilst field results confirm that Cd is generally present at environmentally significant concentrations in the pore waters present in the upper (particularly the oxidation and transitional) zones of the tailings impoundments, subsequent attenuation of Cd appears to be more significant than that predicted on the basis of thermodynamic considerations alone. Field results indicate that iron, on the other hand, is more mobile and of greater direct environmental significance than that predicted on the basis of thermodynamic considerations. Iron in the pore waters from actual tailings impoundments is probably mainly in the form of ferrous iron (Fe(II)), which is stable in the absence of oxygen and is considerably more mobile than ferric iron (Fe(IIII)). The elevated concentration levels of Fe(II) in the field pore waters can possibly be due to:

- incomplete oxidation of ferrous iron arising from the direct oxidation of iron sulphide minerals in the oxidation zone, due to slow reaction kinetics; and/or

- the partial dissolution of relatively reactive primary Fe(II) minerals such as siderite in the lower unoxidised regions of the impoundment.

The relatively high concentration of calcium in the field pore waters at the groundwater interface zone may also be due to the dissolution of reactive primary Ca-bearing minerals such as calcite in the lower unoxidised regions of the tailing impoundment, upon contact with weakly acidic waters migrating from the upper regions.

Table 3.14: Potential environmental significance of constituents in the pore waters from actual sulphide tailings impoundments

A: Minimum field concentrations

Group description	Surface/ oxidation zone	Transitional/ unoxidised zone	Groundwater interface zone
Soluble concentrations exceeding general drinking water criteria by >1000	-	Fe	-
Soluble concentrations exceeding general drinking water criteria by 100-1000	H+	Zn	-
Soluble concentrations exceeding general drinking water criteria by 10-100	Mn, Ni, sulphate, Al, Zn, Cd,	Pb, sulphate, Mn	Mn, sulphate
Soluble concentrations exceeding general drinking water criteria by 1-10	Fe, Ca, Si, TDS	Mg, Si, As, Ni, Cu, Cd, TDS	Fe, Ca, TDS
Soluble concentrations not exceeding general drinking water criteria	Co, Pb, Mg, As, Cl, Na, Cu, K, Cr, Sr	Cl, Na, K, Ca, Al, Co, Cr, Sr, H+	K, Zn, Na, As, Mg, Si, H+

B: Maximum field concentrations

Group description	Surface/ oxidation zone	Transitional/ unoxidised zone	Groundwater interface zone
Soluble concentrations exceeding general drinking water criteria by >1000	Mn, Cd, Fe, Zn, H+	Mn, Cd, Fe	-
Soluble concentrations exceeding general drinking water criteria by 100-1000	Al, Ni, sulphate, Pb	Al, sulphate, H+	-
Soluble concentrations exceeding general drinking water criteria by 10-100	Mg, As, TDS	Mg, As, Ni, Pb, TDS	Mn, sulphate, Fe, Zn, TDS
Soluble concentrations exceeding general drinking water criteria by 1-10	Si, Na, Ca, Cu, Co,	Si, Na, Ca,	Na, Mg, As, Ca, H+
Soluble concentrations not exceeding general drinking water criteria	K, Cr, Cl, Mo, Sr	Cu, Co, K, Cr, Cl, Mo, Sr	Si, Al, K, Cl, Cd, Pb, Mo, Sr, Cu, Cr

Table 3.15 groups and ranks the constituent elements commonly associated with porphyry-type copper sulphide tailings in accordance with potential environmental significance, on the basis of available field results and fundamental thermodynamic considerations. The results of this study indicate that salinity (comprised mainly of sulphate salts) and the individual metals Mn and Fe are likely to be of environmental significance for all porphyry-type copper sulphide tailings. Other components which may be of environmental significance, depending on their concentrations within the specific feed ore, include As, Zn, Cd, B, Mo, Se and, to a lesser extent, Ni, Co, Sb and Si. Acidity may also be of environmental concern for certain ore bodies.

Table 3.15: Generic ranking and grouping of selected elements in pore waters from porphyry-type copper sulphide tailing impoundments on the basis of predicted environmental significance

Group	Constituent components	Measurable indicators
Components likely to be of environmental significance under most conditions	***Major soluble salts:*** Mainly the sulphate salts of Ca and, to a lesser extent, Mg and Na	TDS or EC.
	Metals: Mn, Fe	Individual concentrations
Components which may be of environmental significance for certain deposits or under specific conditions	***Metals:*** As, Zn, Cd, B, Mo, Se> Ni, Cu, Sb, Si	Individual concentrations
	Acidity: H+	pH

3.3 Empirical Characterisation of a Specific Porphyry-Type Copper Sulphide Tailings Sample

In accordance with the generic methodology outlined in Chapter 2, the third step in the prediction of solid waste impacts is quantitative waste characterisation. This step essentially entails derivation of quantitative data pertaining to those properties identified within the previous two steps of the methodology (problem formulation and qualitative waste characterisation) as being of potential environmental significance.

The development and application of a systematic laboratory-scale protocol for the empirical characterisation of a porphyry-type copper sulphide tailings waste has formed part of a two year MSc dissertation project by Maluleke (2006). The main tasks associated with this project phase are outlined in Figure 3.9, and summarised in the following sub-sections of the report (3.3.1 to 3.3.3).

3.3.1 An empirical waste characterisation protocol for porphyry-type copper sulphide tailings

Section 2.3 of this report proposed a generic procedural framework for solid mineral waste characterisation to support predictive modelling, which can then be tailored to specific waste types (see Figure 2.11 in Section 2.3.3). In accordance with this generic framework, empirical waste characterisation methodologies can be broadly categorised into two groups, namely: 1) analytical and static laboratory methods to determine the physio-chemical properties of the wastes (i.e. the inherent properties of the waste *influencing* the potential environmental availability of contaminants and leachate properties); and 2) leach tests which can be directly interpreted in terms of maximum, operationally-defined or time-related availability of contaminants under simulated disposal conditions.

Discussions in Section 3.2 have, furthermore, indicated that the leachate generation properties (in terms of major soluble salts, pH and trace-minor metals) of a porphyry-type copper sulphide tailings will be dictated in the first instance by the relative rates and extents of the acid-generating sulphide oxidation reaction and acid-consuming carbonate and silicate dissolution reactions within the top oxidation zone of the tailings impoundment. As previously discussed, these reactions are mainly slow, kinetically-controlled reactions influenced largely by the rates and extent of oxygen diffusion and hydraulic conductivity within the impoundment. As such, conventional short-term laboratory-scale leach tests (including batch extraction and column leach tests) are unlikely to produce meaningful results in terms of the primary reactions governing the key characteristics (major salts, pH and redox potential) of the pore water within the upper oxidation zone, and will not be warranted in the case of predictive studies for the support of strategic or tactical decisions in the early stages of a project life cycle.

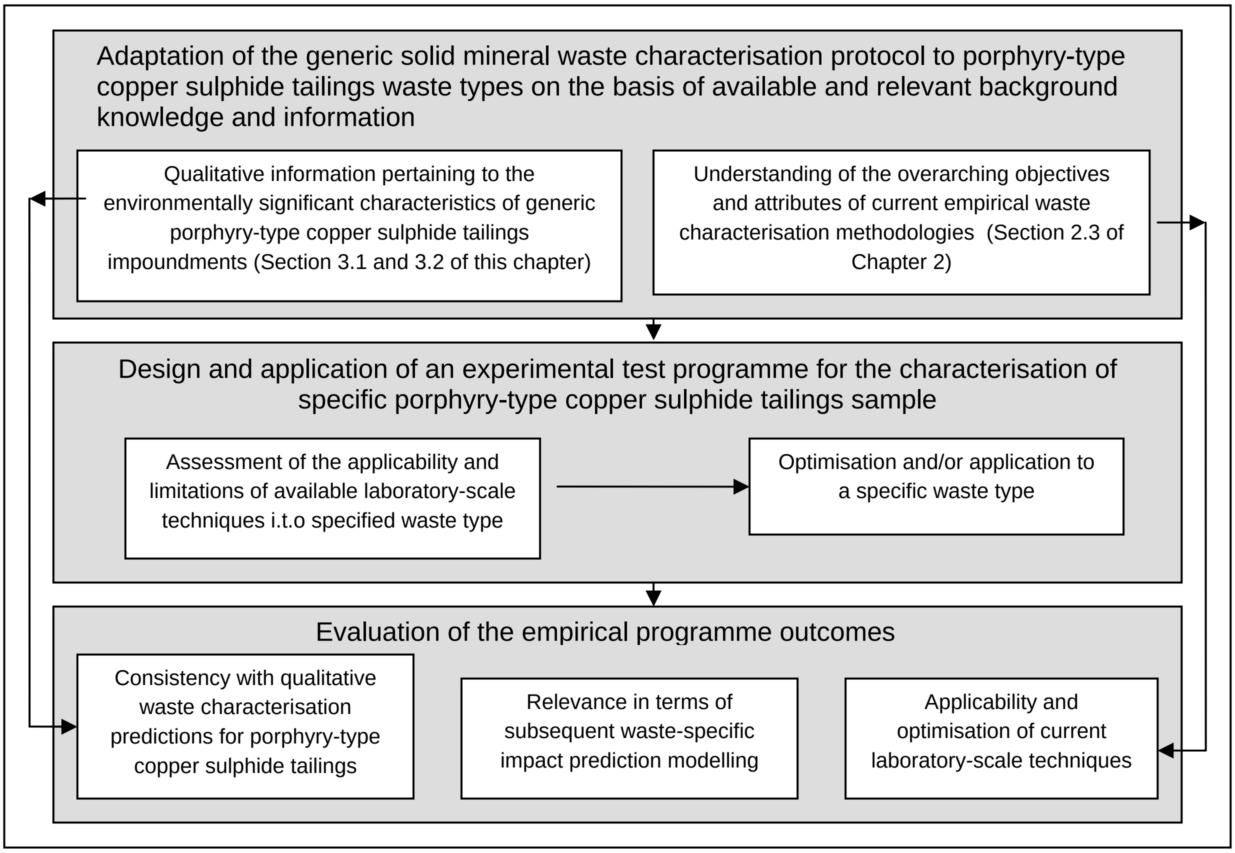


Figure 3.9: Empirical characterisation of a specific porphyry-type copper sulphide tailings sample: project tasks

The scope of work in terms of this particular project phase has thus been limited to the determination of the key physio-chemical properties of porphyry-type copper sulphide tailings using analytical and so-called “static” laboratory waste characterisation methodologies (i.e. waste characterisation methodologies corresponding to level 2 in the generic protocol outlined in Figure 2.11, Section 2.3.3). As summarised in Tables 2.5 and 2.6 in Section 2.3.2 of the report, such methodologies include techniques for the quantification of the relevant physical properties; analytical techniques for quantification of total element concentrations, analytical techniques for the quantification of mineralogical compositions; sequential chemical extraction tests to determine the partitioning or distribution of elements; and tests designed to determine the capacity of a waste to generate or neutralise acid.

An empirical protocol for the specific characterisation of the physio-chemical properties of porphyry-type copper sulphide tailings has been developed on the basis of the qualitative information derived in the previous two sections of this chapter, as well as the overview of current solid waste characterisation tools in Section 2.3.2 of the report, and is presented in Figure 3.10. The section provides a more detailed review and assessment of the relevant empirical waste characterisation methodologies.

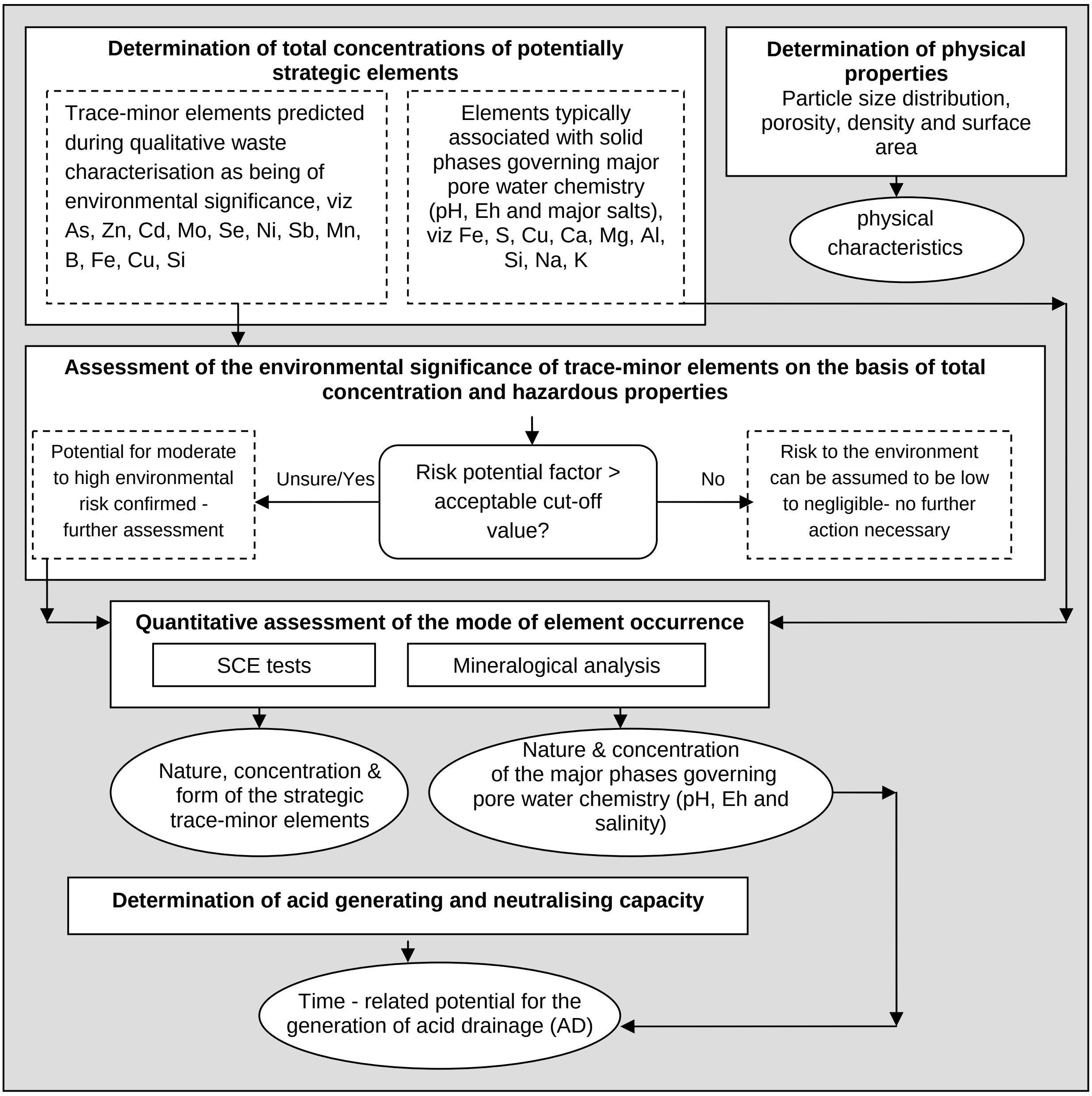


Figure 3.10: Empirical protocol for the characterisation of the key physio-chemical properties of porphyry-type copper sulphide tailings

Techniques for the determination of total element concentrations in solid wastes

Analysis of the total metal and semi-metal concentrations can be carried out using either non-destructive techniques, such as X-ray Fluorescence Spectrometry (XRF), or destructive techniques, which entail complete dissolution of the sample (by means of acid digestion, sintering or fusion) and subsequent analysis of the dissolved species. The most common methods for the determination of metals in digests include Atomic Adsorption Spectroscopy (AAS) and Inductively Coupled Plasma (ICP) techniques. AAS can be conducted in flame (Flame Atomic Adsorption Spectroscopy, FAAS) or graphite furnace mode (Graphite Furnace Atomic Adsorption Spectroscopy, GF-AAS). ICP can be coupled with Optical Emission Spectroscopy (ICP-OES; also termed ICP-ES or ICP-AES), or with Mass Spectroscopy (ICP-MS).

Although expensive, ICP-MS is a particularly useful technique for the analysis of total metal and semi-metals in solid mineral waste, as it is able to rapidly and simultaneously quantify a number of elements (up to 75) at very low concentration levels (detection limit of 0.1ppb), and with relatively few spectral or matrix interferences. In-house investigations have demonstrated a >95% confidence limit for a number of metals and semi-metals (Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Hg, Mg, Mo, Ni, Pb, Sb, Se, Si, Sn, Sr, Ti, V, Zn, Zr) in various solid mineral waste samples, at concentration levels as low as 1 ppb. This technique is, however, not suitable for the accurate and reliable analysis of Fe, Na and K. In the case of these metals, confidence limits of >95%, at concentration ranges of 60ppb, 20ppb and 40ppb for Fe, Na and K respectively, have been achieved using FAAS.

The high temperature combustion furnace (LECO) technique is most commonly used for the determination of total sulphur in solids. Total inorganic sulphur in weathered or aged sulphide tailings is frequently present in a number of forms (sulphate, sulphide and/or elemental sulphur), the selective separation or fractionation of which is generally considered to be problematic (see discussion by Lapakko, 2002). In the case of freshly prepared sulphide tailings, however, the majority of the sulphur is likely to be in the form of unoxidised sulphide (particularly as iron sulphides), with negligible formation of secondary sulphide oxidation species such as elemental sulphur and/or sulphate precipitates.

Mineralogical analytical techniques

Mineralogical analytical techniques can be used to identify the chemical forms or phases in which the constituent components are present within the waste; quantify the proportions in which the various phases occur; and provide information as to the manner in which the phases are distributed (degree of liberation, associations with other minerals etc). Certain techniques allow for the analysis of the chemical and physical properties on a particle level, including identification of non-homogeneities in mineralogy; quantification of grain and particles sizes; and analysis of particle surfaces. The most common methods include X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), SEM coupled with Energy Dispersive Spectrometry (SEM-EDS) and Optical Microscopy. The state-of-the-art in automated mineralogical investigation of mineral ores and concentrates is the QEMSCAN system, developed by CSIRO in Australia, and JKTech’s Mineral Liberation Analyser (MLA). Although very expensive, a particular advantage of these systems is the strong visual and data explorative capabilities, which facilitates meaningful and effective interpretation. In general, mineralogical analysis becomes more difficult, time consuming and expensive on going from qualitative to quantitative analysis, and from bulk to particle level analysis. In accordance with a number of authors (Bermond, 2001; Eary, 1990 and Leinz, 2000), conventional techniques are not sufficiently sensitive for the mineralogical analysis of trace to minor phases in solid mineral wastes. As a result, solid phases containing minor elements have mostly been predicted in solid wastes, but not actually observed.

Sequential chemical extraction (SCE) tests

SCE tests are carried out by subjecting either different samples of the waste material to leachants of various strengths in a series of parallel tests, or by subjecting one sample to differing strengths or types of leachants sequentially. In the former case, it is assumed that each stronger leachant will also extract the total sum of the components from weaker leachants. Usually between three and eight leachants or extractants are used, beginning with the least aggressive-most specific and ending with the most aggressive-least specific. SCE tests have traditionally been developed for providing information pertaining to the partitioning or distribution of trace to minor metals in major soil and sediment phases (see for example Abollino et al., 2001; Bendell-Young et al., 2001; Bermond, 2001; Galan et al. 2002; Garrabrants & Kosson, 2001; Li & Thornton, 2001; Marin et al., 2001; Morera et al., 2001; Mowat & Bundy, 2001; Ngiam & Lim, 2001; Phillips & Chapple, 1995; Prudent et al., 1996; Quevauviller et al.,1997; Stegemann & Cote, 1990; Sutherland, 2002; Tessier & Campbell, 1979; Usero et al., 1998; van Ryssen et al., 1999; Wenzel et al., 2001; Yu et al., 2001). Whilst many of the extractants used in these tests are specific to soil systems, SCE tests have been increasingly applied to solid wastes from chemical and primary metal industries. Of particular relevance to this study is the work by authors such as Carlsson et al. (2002); Dold & Fontbote (2001); Dold (2003); Fanfani et al. (1997); Jaebong (2003); Kontopoulous et al. (1995); Leinz et al. (2000); McGregor & Blows (2002); and Ribet et al. (1995), who have developed and applied modified versions of the traditional SCE tests to sulphide bearing mine wastes (including waste rock and tailings). These "modified" SCE tests essentially involve sequential quantification of the relative quantities of components in as many as 7 different fractions, namely: the water soluble; ion-exchangeable; adsorbed and/or carbonate bound; amorphous oxide bound; crystalline oxide bound; sulphide bound; and residual fractions. Table 3.16 lists possible extractants and the component or phase that they target.

Table 3.16: Summarised list of possible extractants used in SCE tests and associated extracted phases (adapted from Hansen, 2004 and Maluleke, 2006)

Fraction description	Reported extractants	Specific extracted phase or component
Fraction 1a: Waste soluble	Deionised or distilled water	Water soluble
Fraction 1b: Exchangeable components	Potassium chloride, potassium nitrate, calcium chloride, calcium nitrate and magnesium chloride, lithium chloride and cesium chloride.	Exchangeable, neutral salt exchangeable, water soluble or non-specifically adsorbed
	DTPA	Exchangeable and organically bound metals, "precipitates"
	Ammonium acetate and ammonium chloride	Exchangeable metals
Fraction 2: Carbonate bound and/or specifically adsorbed components	Potassium and sodium fluorides	"Adsorbed" metal, [organic matter]
	Lead nitrate and copper acetate	"Specifically bound" metals
	Sodium acetate in acetic acid (pH5)	Chemically adsorbed metals and elements present as or occluded in carbonate minerals
	Acetic acid	Carbonates, some iron and manganese oxides, "acid-soluble" metals, "specifically bound" metals and decomposed organic matter
	Sodium and potassium pyrophosphate	Organically bound metals [some aluminium, iron and manganese oxides, some metal carbonates and copper sulphides]
Fraction 3: Fe/Mn oxide bound	Hydroxylamine hydrochloride	Manganese oxides (Fe oxides)
	Sodium citrate	Iron oxides
	Oxalic acid	Free oxides and primary minerals
	EDTA	Carbonates, "inorganic precipitates", amorphous and crystalline oxides and hydroxides of iron, organically bound metals
	Acid ammonium oxalate [1]	Iron and aluminium oxides, hydroxides and oxyhydroxides, aluminium and iron from organic complexes, zinc and copper carbonates, [sulphides]
Fraction 4: Organic/Sulphide bound	Sodium dithionate	Iron oxides, organic-iron complexes
	Sodium hydroxide	Organic matter, some metal carbonates
	Sodium hypochlorite	Organic matter, (sulphides)
	Hydrogen peroxide with nitric acid	Organic matter, (sulphides, carbonates and oxides)
Fraction 5: Residual	Strong, mineral acids	Residual minerals
Note 1: This extractant can be used in two sequential phases to differentiate between amorphous iron oxides/hydroxides such as ferrihydrite and crystalline iron oxides such as goethite and haematite, where: • Tamms Acid oxalate solution dissolves all manganese oxide/hydroxide and amorphous iron oxide/hydroxide compounds. • Shumans reagent (TAO leach under high temperature and in the presence of light and ascorbic acid) dissolves all crystalline iron oxides, as well as crystalline aluminium oxides such as gibbsite and bauxite.		

SCE tests on solid mineral wastes provide quantitative data pertaining to the forms in which major components occur, and the manner in which of the trace to minor components are associated with these major minerals (i.e. their mode of occurrence), and can thus play a key role in terms of complementing (and overcoming the associated limitations) of conventional mineralogical techniques. The SCE results can also be used to infer information pertaining to the potential chemical reaction mechanisms and parameters controlling the mobility of elements in a disposal scenario. As indicated in Table 3.17, each fraction can be assumed to representing a different mode of occurrence and potential controlling chemical reaction mechanism.

Table 3.17: Potential modes of occurrence and leach behaviour on the basis of SCE test results

Fraction	Potential mode of element occurrence	Potential mechanism and parameters controlling element mobility
Water soluble	Present as highly reactive and liberated salts	Mobility will be instantaneous or rapid and will be dependant only on the concentration in this fraction
Exchangeable components	Weakly adsorbed onto clay minerals, iron and magnesium oxides/hydroxides, organic matter and other colloids.	The mobilisation of exchangeable components from solid will most likely occur as a result of rapid ion-exchange reactions, and will be dependant on the soluble salt concentrations and pH
Carbonate bound and/or specifically adsorbed components	Present as or occluded in carbonates and/or chemically adsorbed onto surfaces of simple and complex oxides of iron, manganese and aluminium compounds (simple and complex oxides).	Mobility is likely to be controlled by the rate and extent of carbonate and oxide dissolution/precipitation or by surface adsorption reactions, and will be dependant on pH.
Fe/Mn oxide bound	Present as or occluded in manganese and iron oxides	Mobility is likely to be controlled by rate and extent of Fe and Mn oxide dissolution/precipitation, and will be largely dependant on pH and Eh
Sulphide bound	Present as or occluded within organic matter and/or sulphide minerals	Mobility will be governed by the rate of organic matter/sulphide mineral oxidation, which will be largely controlled by oxygen diffusion
Residual	Present as or occluded in stable primary mineral phases	Element phases are likely to either be inert, or mobilised at extremely slow rates under most disposal conditions

SCE test results can also be interpreted in terms of the relative availability of elements for release into the environment. Water-soluble and exchangeable components can be expected to be readily available for release in the short-term, whilst the environmental availability of components that are associated with the sulphide or residual fractions is likely to be negligible. Together with an appreciation of the hazard potential of individual elements, information on the relative availabilities of the various waste contaminants can be used to identify possible strategic components in terms of potential environmental significance. Both Galan, 2002 and Hansen, 2004 have developed ranking systems and associated graphical representations for the identification of strategic elements on the basis of total environmental availability, as inferred from SCE test results.

Despite the wealth of information that can be derived from SCE tests, there is currently considerable uncertainty regarding the accuracy of the quantitative results. Such uncertainty is due mainly to concerns regarding the specificity (or lack thereof) of the various extractants, as well as potential re-partitioning of components during the extraction tests. Furthermore, many variables will affect the performance of the extractants in liberating specific mineral phases, and test conditions applicable to one material may not be applicable to others. Operationally-defined variable which can influence the selectivity and accuracy of the extraction procedures include the chemical extractants employed; the pH of the extracting solution; the solution/solid ratio; the number of extraction steps; and the extraction time and nature of contact. Unless verified by other characterisation tests, the results of the SCE tests should be considered as only semi-quantitative estimates of metal partitioning.

Techniques for assessing the acid generating potential of sulphide-bearing wastes

The capacity of a waste to generate or neutralise acid will be dependant on the relative concentrations of acid-producing and acid-consuming components, and can thus be considered an inherent property or characteristic of a particular material.

As already discussed, acid drainage (AD), also referred to as acid mine drainage (AMD) or acid rock drainage (ARD), is a well-known problem associated with sulphide bearing wastes, which has prompted the development and application of a number of so-called static tests for estimating the acid generating potential of such wastes. These tests can be broadly categorised into Acid Base Accounting (ABA) methods and Net Acid Generating (NAG) methods.

- *Acid Base Accounting (ABA) tests:* These tests entail calculation of the acid generating potential by comparing the wastes maximum acid production potential (referred to as AP, MPA or APP) with its maximum acid neutralisation potential (NP) or capacity (ANC). The maximum acid production potential (MPA, AP or APP) is based on the theoretical amount of acid (kg/t H_2SO_4) that will be produced if the measured total sulphur or sulphide content is present in the form of pyrite, and oxidised in accordance with the equation:

  $$FeS_2 + 3.75O_2 + 3.5H_2O \leftrightarrow Fe(OH)_3 + 2H_2SO_4$$

  The neutralisation potential (NP or ANC, also measured in kg/t H_2SO_4) is determined by adding excess acid to a sample, heating or boiling the solution so as to dissolve all acid neutralising components (carbonates, oxides/hydroxides and silicates), and then back titrating to a set pH value to determine how much acid was neutralised. The acid generating potential is subsequently expressed as the Net Neutralisation Potential (NNP), the Net Potential Ratio (NPR) or the Net Acid Producing Potential (NAPP), and the sample classified accordingly. The various classification criteria for the acid generating potential on the basis of ABA test results are presented in Table 3.18.

Table 3.18: Classification criteria for acid generation potential of mining and minerals processing wastes: ABA tests

	NPR	NNP	NAPP
Calculation	NP/MPA	NP-MPA	MPA-NP
Acid generating	NPR<1	NNP<-20	NAPP>20
Non-acid generating	NPR>3	NNP>20	NAPP<-20
Potentially acid generating	1< NPR < 3	-20 < NNP < 20	-20< NAPP< 20

The original ABA test method, developed by Sobek et al. (1978), has undergone several adaptations and modifications, particularly in the last decade (see overviews by Crock et al., 1999; Miller et al., 1991; Mills, 1998; US EPA, 1994; Usher et al., 2003(a&b). A significant modification to the original Sobek (1978) method is the establishment of a requisite digestion end-point pH range to control acid addition, rather than relying solely on the subjective “fizz test” (Lappako, 2002; Lawrence and Wang, 1997; AMIRA, 2002). Another important modification involves the addition of hydrogen peroxide prior to back-titration, in order to ensure complete oxidation of Fe(II) arising from the hydrolysis of siderite ($FeCO_3$) and/or oxidation of pyrite during acid digestion (Skousen et al., 1997; Weber et al., 2004a & 2004b). Several versions of these modified Sobek ABA test method have, however, been described – with different static test methods leading to significant variations in the ANC values for the same sample (Mills, 1998). The ANC variability for a given sample is reported to be influenced mainly by differences in particle size reduction; amount and concentration of acid addition; the back-titration end-point; and the sample mineralogy (Lapakko, 2002; White et al., 1999).

- *Net Acid Generation (NAG) tests:* An alternative technique for the direct measurement of the net acid generating potential, i.e. not entailing prior analysis of sulphur species, is the Net Acid Generation (NAG) test method. This methodology involves the treatment of waste with hydrogen peroxide to simultaneously dissolve both acid producing and acid neutralising components, followed by the measurement of the pH (termed NAG_{pH}) and back-titration firstly to a pH of 4.5 (which accounts for acidity due to oxidation and free acid), and finally to a pH of 7 (which accounts for acidity due to secondary precipitate formation). As in the case of the ABA technique, several variations of the NAG technique have been applied to a variety of mine waste materials (see for example Finkelman & Giffin, 1986; Miller et al., 1991; Mills, 1998; Trans et al., 2003; Weber et al., 2004b). The three main NAG test procedures are the single addition NAG test, the sequential NAG test, and the kinetic NAG test. The sequential NAG technique entails repeated treatment of the solid residue with fresh H_2O_2 solution until a NAG_{pH} of ≥ 4.5 is obtained, and is generally applied to samples with pyritic –S contents of > 1%. The kinetic NAG test involves monitoring the rate of change in the solution pH and temperature during the single addition NAG tests, the time-related variation of which provides and indication of the kinetics of sulphide oxidation and acid neutralisation reactions and an estimation of the likely lag time for acid generation in a disposal scenario. Classification of the acid generating potential of the samples on the basis of the NAG test results are presented in Table 3.19.

Table 3.19: Classification criteria for acid generation potential of mining and minerals processing wastes: NAG tests

Classification	Parameters
Acid neutralising	NAG = 0 kg/t H_2SO_4; and $NAG_{pH} > 7.5$
Non-acid generating	NAG = 0 kg/t H_2SO_4; and $4.5 \leq NAG_{pH} < 7.5$
Low to moderately acid generating	NAG at pH 4.5 < 5 kg/t H_2SO_4 ; and NAG at pH 7.0 = 2-10 kg/t H_2SO_4 ; and $NAG_{pH} < 4.5$
Highly acid generating, but with slow kinetics	NAG > 20 kg/t H_2SO_4; and $NAG_{pH} < 4.5$; and Time to temperature peak and pH stabilisation > 3 hours
Potential for high and rapid acid generation	NAG > 20 kg/t H_2SO_4; and $NAG_{pH} < 4.5$; and Time to temperature peak and pH stabilisation < 15 minutes

3.3.2 Design and application of an experimental test programme for the preparation and characterisation of specific porphyry-type copper sulphide tailings sample

Preparation of a porphyry-type copper sulphide tailings sample

A sample of fresh, unoxidised tailings was prepared on a laboratory-scale at UCT from a bulk sample of run-of-mine ore originating from the Bingham Canyon copper porphyry body located near Salt Lake City. This ore body contains chalcopyrite as 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, 1994). Generally, pyrite and to a lesser extent chalcopyrite, bornite and molybdenite are the primary minerals contributing to acid production in the 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. 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, 1994).

The flotation cell used for the laboratory-scale batch flotation test is a modified 3 *l* Leeds batch flotation cell. 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 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. The tailings were filtered and a sample of the liquid phase – the tailings discharge liquor – submitted for analysis. The solids were oven dried at < 40°C to prevent decomposition of minerals contained in the samples, and then rotary split to obtain representative sub-samples using a rotary sample divider.

Characterisation of the tailings discharge liquor

The tailings discharge liquor was submitted for analysis of sulphate by means of high performance liquid chromatography (HPLC); dissolved Fe, Na and K by means of FAAS; and dissolved Ca, Mg, As, Cu, Zn, Mo, Al, Mn, Cd, Ni, Sb, Se and Ge using the ICP-MS technique.

Characterisation of the physical properties of the solid tailings

Solid sample were submitted for particle size distribution analysis using a Malvern Mastersizer. Surface area and pore size distribution was determined by means of a BET (Brunauer-Emmet-Teller) analyser.

Analysis of total element concentrations in the run-of-mine ore and solid tailings

Total sulphur in the solid tailings sample was determined using a LECO analyser

For the determination of metals and semi-metals, ore and tailings samples were digested in 3 stages - using hot solutions of HF (Stage 1), aqua regia (stage 2) and HF/$HClO_4$ (stage 3). The concentration of elements in the digestates were determined using FAAS (for Fe, K and Na) and ICP-MS (for other metal and semi-metal constituents, namely: Cu, Si, Al, Mg, K, Ca, Na, Mn, Co, Cr, Zn, Cd, As, Mo, Ag, Pb, V, Be, Ni, B, Sb, Se). This list included, but was not limited to, all the requisite elements listed in Figure 3.10.

Mineralogical analysis

Quantitative X-ray Diffraction (XRD) analysis was carried out at the University of Pretoria, using a PANalytical X'pert Pro with X'celerator detector.

Sequential chemical extraction (SCE) tests

In view of the uncertainties and controversies associated with currently available test procedures, two potentially suitable SCE test protocols were selected to test their consistency and suitability. The first sequential extraction scheme (A) was consistent with the modified seven step procedure adopted by Dold & Fontboté (2002) and Dold (2003) for the study of sulphide-rich copper mine tailings. The second sequential extraction scheme (B) used in this study was slightly modified from Ribet et al. (1995); Hall et al. (1999) and Carlsson et al. (2002). These two protocols are described in detail in Appendix H1 and summarised in Tables 3.20 and 3.21 respectively. These test protocols included selected kinetic tests to investigate the effect of extraction period on the extent of Mn and Fe-oxide dissolution. The supernatants or extracts from each of the SCE stages were analysed as for the acid digestates. Comparison with total element concentrations and results of the XRD analysis, as described above, provided further validation of the SCE results.

Table 3.20: Sequential extraction scheme A adopted for sulphidic mine tailings (Dold & Fontboté, 2002; Dold, 2003)

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 and Martin, 1986; Fonseca and da Silva, 1998
F3: Amorphous and poorly crystalline Mn, Fe-oxides	20 ml 0.2 M NH_4 –oxalate, pH 3.0 adjusted with 0.2 M oxalic acid, 1-4 hrs in darkness	MnO_2, secondary jarosite, ferrihydrite, schwertmannite	Han *et al.*, 2001; McGregor & Blowes, 2002
F4: Crystalline Mn, Fe-Oxide	20 ml 0.2 M NH_4 –oxalate, pH 3.0 adjusted with 0.2 M oxalic acid, at 80 °C, 2 hr	Goethite, hematite, magnetite	Ribet *et al.*, 1995; Han *et al.*, 2001; McGregor & Blowes, 2002
F5: Secondary sulphides and organics	5 ml 35% H_2O_2, in water bath, 1 hr	Covellite, chalcocite, digenite	Sondag, 1981
F6: Metals in sulphide phase	750 mg $KClO_3$ and 5ml 12 M HCl, followed by 4 M HNO_3 at 90°C	Pyrite, chalcopyrite, galena, covellite	Chao and Sanzolone, 1977; Hall *et al.*, 1996
F7: Residue	Aqua Regia (HCl, HNO_3), HF, $HClO_4$	Silicate minerals	Tessier *et al.*, 1979

Table 3.21: Sequential extraction scheme B (modified after Ribet et al., 1995; Hall et al., 1999; Carlsson 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 and Martin, 1986; Fonseca and 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 Mn, Fe-oxides	20 ml 0.25 M $NH_2OH.HCl$ in 0.25 M HCl, pH 2.0, 50 °C, shaking for 2-12hr	MnO_2, secondary jarosite, ferrihydrite, schwertmannite	Chao and Zhou, 1983; Hall *et al.*, 1996
F5B: Crystalline Mn, Fe-Oxide	30 ml 2 M $NH_2OH.HCl$ in 25% CH_3OOH, pH 2.0, shaking for 3-24 hr, 90 °C	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	Pyrite, chalcopyrite, galena, covellite	Chao and Sanzolone, 1977; Hall *et al.*, 1996
F7: Residue	Aqua Regia (HCl, HNO_3), HF, $HClO_4$,	Silicate minerals	Tessier *et al.*, 1979

Acid generation tests

As in the case of the SCE testwork, a variety of methods and test conditions have been investigated here, so as to identify opportunities to optimise the empirical assessment of the acid generating potential of porphyry-type copper sulphide tailings. These tests are described in detail in Appendix H2 and include:

- A standard ABA test, in accordance with the method of Sobek et al. (1978)
- Two modified ABA tests, both with a H_2O_2 addition step for Fe(II) oxidation. One test method involved a single addition of H_2O_2, based on the method of Skousen et al. (2000). The second method entailed incremental H_2O_2 additions, in accordance with recommendations by Weber et al. (2004a).
- A single NAG test
- A sequential NAG test
- A kinetic NAG test

3.3.3 Evaluation and discussion of the empirical characterisation results

This section presents and interprets the results of the experimental testwork programme, with specific emphasis on the applicability and optimisation of current laboratory-scale techniques; the consistency of the empirical results with the qualitative waste characterisation predictions (Section 3.2); and the relevance of the empirical waste characterisation outcomes in terms of subsequent waste-specific impact prediction modelling.

Tailings discharge liquor composition

The composition of the tailings discharge liquor is compared with available literature data in Table 3.22.

Table 3.22: Tailings discharge water composition porphyry-type copper sulphide tailings sample

	Results from this testwork programme	Reported data (after Coetzer et al., 2003; Ng'andu, 2001; Mwale et al., 2005)
Ca	464	45-653
Mg	3.6	36-72
K	24.6	24
Na	13	120
SO_4^{2+}	280	309-1989
Fe	-	90-1100
As	3.3	-
Cu	1.4	300-17200
Zn	55	<10-340
Mo	19	-
Al	56	-
Mn	1.2	160-290
Cd	0.07	-
Ni	18	340
Sb	0.5	-
Se	24	-
Ge	0.07	-
Initial pH	10.6	8.5-11.3
Settled pH	7.6	-
All values except pH in ppm (mg/l)		

These results indicate that the tailings discharge water is comprised largely of calcium and sulphate, with lesser amounts of potassium and sodium – the concentrations of which are fairly consistent with those values reported in the literature. In the case of magnesium and other trace-minor metals, however, the concentrations in the laboratory-scale flotation discharge liquor are somewhat lower than reported values. Furthermore, although a pH of 10.6 was recorded directly after flotation, this dropped fairly rapidly to values of between 7.2 and 7.9 (average 7.6) on standing. This can probably be attributed to the formation of bicarbonate due to dissolution of atmospheric CO_2, and may be indicative of the relatively low neutralising capacity of the tailings in the short-term.

Physical properties of the solid tailings

The results of the physical characterisation tests indicate that the solid tailings sample, as generated in the laboratory, has an absolute density of 2.9 g/cm^3, which is within the range of values reported for typical base metal sulphide tailings (2.2-3.5 g/cm^3). A comparison of the particle size distribution data in Table 3.23 indicates, however, that the laboratory-prepared tailings material is somewhat finer than that typically generated on a commercial plant.

Table 3.23: Comparative particle size distribution data porphyry-type copper sulphide tailings sample

Literature values (Bulatovic et al., 1998)	Particle size distribution of the laboratory-prepared sulphide tailings sample
40-55% passing 74µm	54% passing 20µm
80% passing 140-320 µm	80% passing 74µm

The tailings sample has a BET surface area of 7.4 m^2/g; a total pore volume of 0.018 cm^3/g; and an average pore diameter of 97.6 A

Total element concentrations in the run-of-mine ore and flotation tailings

Table 3.24 compares the total element concentrations in the run-of-mine ore and tailings with the generic predictions in Section 3.2.

For the most part the empirical element concentrations in the specific copper sulphide ore and tailings are consistent with the predicted values. Notable exceptions include Al, Na, Se (all of which are present in lower concentrations than predicted) and B (present in significantly higher levels than those predicted). Although consistent with the predicted ranges for the run-of-mine ores, the levels of Ni and Co in the flotation tailings are slightly higher than predicted concentrations. This indicates that the deportment of these elements to the tailings during flotation is higher than that predicted (distribution factors of 0.1-0.3). This may be due to the fact that these elements occur within the ore body in the form of oxide compounds (rather than sulphides), or as inclusions within pyrite gangue.

Table 3.24: Total element concentrations in the run-of-mine ore and flotation tailings sample

Element	Results from this testwork programme		Predicted values (see Section 3.2, Tables 3.7 & 3.8)	
	Ore	Tailings	Ore	Tailings
Major sulphide-forming elements (%)				
Cu	0.21	0.12	0.5-1.0	0.08-0.15
Fe	11.6	7.2	1-10	0.8-9.5
S	10.2	3	2-11	1-11
Major rock-forming elements (%)				
Si	20.1	23	21-34	21-35
Al	0.44	0.49	4.0-10	4.0-10
Mg	0.2	0.32	0.2-3	0.2-2.6
K	1.66	1.3	0.3-3.4	0.3-3.5
Ca	0.33	0.91	0.4-4	0.4-4.5
Na	0.042	0.045	0.3-3	0.3-3.2
Trace-minor elements (ppm)				
Mn	958	1244	100-2000	100-2000
Co	18.3	18.5	2.5-50	0.3-15
Cr	232	269.7	10-200	10-200
Zn	129	117.7	150-1600	15-500
Cd	0.8	1.35	2-200	0.2-60
As	56	27.9	5-1800	2-550
Mo	23.7	25.5	15-1500	1-500
Ag	2.2	1.47	1.0-70	0.2-10
Pb	46	36.0	30-300	5-100
V	22.8	37.1	15-300	15-300
Be	0.9	1.07	0.5-30	1-30
Ni	54	109.2	8-150	1-50
B	5563	5938	50-1000	50-1000
Se	n.d	n.d	10-100	1-30
Sb	4.6	4.5	2-200	0.2-62

Mineralogical analysis of the solid tailings sample

The results of the XRD analysis are presented, together with predicted values, in Table 3.25. In terms of the mineral groups, there is a reasonable correlation between the predicted and experimental results, although the minor gangue minerals (comprised largely of haematite) are present in significantly higher concentrations than predicted. As expected the XRD technique is insufficiently sensitive to identify and quantify the forms of the trace to minor sulphide ore and lithophilic gangue elements.

Table 3.25: Quantitative XRD characterisation of the tailings sample

Mineral		Analytical results	Predicted values
Sulphide minerals			
Chalcopyrite	$CuFeS_2$	0.5 ± 0.13 %	0.08-0.2 %
Pyrite	FeS_2	2.9 ± 0.21 %	2-18 %
Total sulphide minerals		3.4 ± 0.34 %	2-18 %
Silicate gangue minerals			
Quartz	SiO_2	53 ± 1.2 %	35-45 %
K-Feldspar (Sanidine)	$KAlSi3O_8$	9.8 ± 0.75 %	20-25 %
Muscovite	$(K,NH_4,Na)Al_2$ (Al, Si)4$O_{10}(OH)_2$)	9.3 ± 0.81 %	10 %
Chlorite	$(MgFe)_5Al(Si_3Al)O_{10}(OH)_8$)	15.6 ± 1.5 %	
Total silicate gangue minerals		88 ± 18.3 %	82-96 %

Mineral		Analytical results	Predicted values
Carbonate gangue minerals			
Calcite	$CaCO_3$	2.4 ± 0.51 %	Mainly calcite with lesser amounts of dolomite, ankerite and/or siderite
Siderite	$FeCO_3$	2.6 ± 0.48 %	
Ankerite	$Ca(Mg,Fe)(CO_3)_2$	trace	
Dolomite	$CaMg(CO_3)_2$	trace	
Magnesite	$CaMg(CO_3)_2$	trace	
Total carbonate gangue minerals		5.0 ± 0.99 %	0.5-4 %
Trace – minor gangue minerals			
Haematite	Fe_2O_3	4.2± 0.30 %	
Goethite	α-FeO(OH	trace	
Pyrolusite	MnO_2	trace	
Total trace to minor gangue minerals		> 4.2± 0.30 %	1-7 %
Total lithophilic gangue minerals		97.2 ± 19.6 %	84-98 %

Sequential chemical extraction testwork

The results of the sequential chemical extraction testwork are presented in Tables 3.26 A and B.

Table 3.26A: Sequential chemical extraction testwork results: Test protocol A

Element	% of total extracted									
	F1A	F2A	F3A	F4A	F3A +F4A	F5A	F6A	F5A+F6A	F7A	Total
Major sulphide-forming elements										
Fe	0.00	0.41	12.71	11.39	24.10	1.63	25.28	26.91	46.78	98.20
Cu	0.00	10.44	15.74	5.05	20.79	45.85	40.80	86.66	0.00	117.88
Major lithophilic gangue-forming elements										
Si	0.00	0.08	0.24	0.52	0.76	0.09	0.42	0.51	92.45	93.81
K	1.28	0.41	6.12	1.42	7.54	0.05	0.00	0.05	87.41	96.69
Ca	3.37	21.98	0.22	0.19	0.41	18.88	20.67	39.55	14.35	79.65
Al	0.05	1.18	3.55	5.82	9.37	0.20	10.33	10.53	84.77	105.90
Mg	3.90	14.80	6.03	9.09	15.12	1.03	20.27	21.30	51.91	107.03
Trace-minor lithophilic (gangue-forming) elements										
Mn	0.00	18.33	38.75	26.85	65.59	7.40	12.14	19.53	12.22	115.76
Cr	0.00	0.33	1.19	1.93	3.11	0.33	104.93	105.27	5.93	114.57
V	0.00	0.00	2.70	2.61	5.31	0.00	75.47	75.47	21.56	102.43
Be	0.00	0.93	28.04	18.69	46.73	0.00	0.00	0.00	9.35	56.07
Trace-minor chalcophilic (sulphide-forming) elements										
Zn	0.00	24.64	33.98	19.54	53.53	6.80	18.69	25.49	9.35	113.00
Ni	0.01	10.99	10.07	4.30	14.38	2.11	78.75	80.86	6.23	111.72
Pb	0.00	8.06	15.83	7.22	23.06	20.83	50.00	70.83	8.06	111.11
As	0.00	0.72	0.00	0.00	0.00	0.00	39.43	39.43	60.93	103.94
Mo	0.39	0.02	1.80	0.71	2.51	0.16	101.96	102.12	6.27	109.80
Co	0.00	37.30	45.41	12.97	58.38	5.30	0.08	5.37	3.24	102.70
Ag	0.00	0.00	0.00	0.00	0.00	20.41	74.83	95.24	12.24	108.84
Cd	0.00	44.44	17.04	4.44	21.48	29.63	14.81	44.44	3.70	111.11
F1A: Water soluble; F2A: Exchangeable and carbonate ; F3A: Amorphous Fe-oxide; F4A: Crystalline Fe-oxide; F5A: Organic matter and secondary Cu-sulphide; F6A: Primary sulphides; F7A: Residual (silicates).										

Table 3.26B: Sequential chemical extraction testwork results: Test protocol B

Element	% of total extracted									
	F1B	F2B	F3B	F2B+F3B	F4B	F5B	F4B+F5B	F6B	F7B	Total
Major sulphide-forming elements										
Fe	0.00	0.70	0.2	0.82	5.03	11.28	16.31	28.65	51.39	97.17
Cu	0.00	10.78	1.88	12.66	2.05	10.69	12.75	58.51	0.86	84.77
Major lithophilic gangue-forming elements										
Si	0.00	0.06	0.21	0.27	0.08	0.83	0.91	0.53	92.86	94.57
K	0.93	0.94	0.41	1.36	0.51	2.79	3.30	0.00	100.15	105.74
Ca	3.59	22.16	5.97	28.12	11.77	16.47	28.24	29.40	8.66	98.01
Al	0.04	1.34	0.26	1.60	1.78	6.26	8.04	28.50	76.51	114.70
Mg	3.62	14.40	1.59	15.99	4.12	8.87	12.99	24.92	51.72	109.21
Trace-minor lithophilic (gangue-forming) elements										
Mn	0.00	18.09	5.31	23.39	19.86	20.74	40.59	4.10	33.28	101.37
Cr	0.00	0.74	0.37	1.11	1.48	2.97	4.45	87.50	21.51	114.57
V	0.00	0.00	0.00	0.00	0.00	0.00	0.00	53.91	56.60	107.82
Be	0.00	1.87	2.80	4.67	15.89	13.08	28.97	12.15	46.73	91.59
Trace-minor chalcophilic (sulphide-forming) elements										
Zn	0.00	23.79	4.25	28.04	10.20	21.24	31.44	23.79	28.89	111.30
Ni	0.00	9.16	2.75	11.90	4.21	0.00	4.21	94.32	0.00	109.89
Pb	0.56	7.50	5.00	12.50	3.89	41.67	45.56	20.56	17.22	97.22
As	0.00	0.00	0.00	0.00	0.00	21.51	21.51	50.18	46.59	118.28
Mo	0.20	0.00	0.00	0.00	0.39	9.02	9.41	86.27	15.69	113.73
Co	0.02	35.14	7.03	42.16	13.51	15.14	28.65	29.19	5.19	102.70
Ag	0.68	0.00	0.00	0.00	6.80	61.22	68.03	20.41	8.84	95.24
Cd	0.00	44.44	7.41	51.85	29.63	7.41	37.04	3.70	0.00	96.30

F1B: Water soluble; F2B: Exchangeable; F3B: Carbonate; F4B: Amorphous Fe-oxide; F5B: Crystalline Fe-oxide; F6B: Secondary and primary sulphides; F7B: Residual (silicates).

The relative consistency between results from the two SCE protocols (A and B) indicates that the differences in the selected reagents and tests conditions (see Tables 3.20 and 3.21) have little effect on the distribution behaviour of elements to the various fractions. Overall metal recoveries (with respect to the total element concentrations resented in Table 3.24) for both SCE protocols are between 97 and 115% - providing further evidence of the reliability and consistency of both these protocols in terms of determining the relative distributions of elements to experimentally-defined extraction phases or fractions.

The interpretation of these results in terms of the potential mode of element occurrence is, however, fraught with uncertainties and discrepancies. In particular, in accordance with the results in Table 3.26 a number of lithophilic oxide-forming elements such as Ca, Mg, Mn and, in particular, Cr and V, are extracted to a significant extent during the so-called “sulphide" extraction step. This indicates that the reagents and extraction conditions used in this step are not selective to sulphide minerals, but will also result in at least partial extraction of relatively stable oxide minerals (such as chromites), as well as acid-soluble silicates. Similarly, the “Fe, Mn-oxide” extraction steps result in partial dissolution of a number of other elements, such as Pb, Cu, Zn, Cd, typically associated with sulphide phases. Once again, this is indicative of the fact that the reagents and test conditions used in this step may also lead to at least partial dissolution of elements present as sparingly soluble sulphates (e.g. anglesite, $PbSO_4$ or barite, $BaSO_4$), or base metal oxides (e.g. cuprite, Cu_2O). Poor selectivity of the various SCE steps may also be due to incomplete extraction of specific phases within the short time periods commonly applied. Kinetic tests by Maluleke (2006) have shown that the leach periods specified in the literature for the extraction of Fe, Mn-oxides do not result in complete extraction of crystalline Fe-oxide phases in the porphyry-type copper sulphide tailings. These oxides are then recovered during subsequent extraction steps and erroneously reported as iron sulphides. Evidence for this is provided in Table 3.27, which provides a comparison of mineral phase concentrations derived from the SCE test results (Table 3.26) with the XRD results, as reported in Table 3.25.

Table 3.27: Comparative mineralogical data for selected elements porphyry-type copper sulphide tailings sample

Element	Mineral phase	XRD analysis (%)	Predicted from SCE testwork results	
			Value	Derivation
Cu	Chalcopyrite $CuFeS_2$	0.32-0.58	0.2-0.3%	58-87% Cu reports to the sulphide fraction
	Cu_2O	n.d.	171-277 ppm	13-21% Cu reports to the Fe, Mn- oxide fractions
Fe	Pyrite (FeS_2)	2.71-3.13	4.1-4.5%	27-29% Fe reports to the sulphide fraction
	Haematite (Fe_2O_3)	3.9-4.5	1.2%	11% Fe reports to the crystalline Fe, Mn- oxide fraction
	Siderite ($FeCO_3$)	2.2-3.1	742-1187 ppm	0.4-0.8% Fe reports to the water-soluble and ion-exchangeable/carbonate fractions
Ca	Calcite ($CaCO_3$)	1.92-2.94	0.6-0.7%	25-31% Ca reports to the water-soluble and ion-exchangeable/carbonate fractions
	Dolomite ($CaMg(CO_3)_2$)	trace	78-82 ppm	19-20% Mg reports to the water-soluble and ion-exchangeable/carbonate fractions
Mn	Rhodocrosite (MnCO3)	n.d.	390-624 ppm	18-23% Mn reports to the water-soluble and ion-exchangeable/carbonate fractions
	Pyrolusite (MnO_2)	trace	807-1300 ppm	41-66% Mn reports to the Fe, Mn-oxide fractions

Discrepancies between the XRD results and those predicted from the SCE test results indicate that further work on the selectivity of the various extraction steps during SCE is still required in terms of deriving quantitative data pertaining to the forms in which elements occur within solid mineral wastes. Nevertheless, these results provide valuable information pertaining to the forms, and approximate concentrations, of trace-minor element phases which are difficult to detect and quantify using conventional mineralogical techniques.

As discussed in the previous sub-section (Section 3.3.2), the results from SCE tests can also be interpreted in terms of the relative availability of elements for release into the environment in a disposal scenario – rendering this technique a useful tool for the identification of strategic elements in terms of environmental significance. Table 3.28 ranks and screens the elements in the porphyry-type copper sulphide tailings sample, on the basis of SCE testwork results. Specifically SCE results have been used to predict the likely reactivity of the elements in the oxidation layer over the long-term, as well as the potential mobility of relatively soluble elements in the lower unoxidised regions of an impoundment through reaction with acidic pore water migrating from the upper layers. Detailed calculations are provided in Appendix I.

The relatively high environmental significance of Mn and S (soluble sulphate), is consistent with the generic predictions summarised in Table 3.15. The relative insignificance of Fe for this particular tailings sample can be attributed to the low concentration of “available” iron in the water-soluble, exchangeable and carbonate SCE test fractions. This is, however, in contradiction to the XRD analytical results (see Table 3.27)

Table 3.28: Screening and ranking of potentially strategic elements on the basis of SCE data porphyry-type copper sulphide tailings sample

Group description	Strategic elements		
	On the basis of the potential reactivity of primary phases in the oxidation zone	On the basis of secondary attenuation of mobilised elements	On the basis of the potential acid hydrolysis of primary phases in the unoxidised layer
I: Very high environmental significance	None	None	None
II: High environmental significance	Fe>Mn, Cu > S >As	Mn > S	Mn> S
III: Moderate environmental significance	Ni, Pb, Mo, Ag, Sb, Cd> Cr	Ni	Ni> Cd> Cu
IV: Low to negligible environmental significance	Al, Si, K, Zn, Ca, Co, Mg, Be, V, Se	Al, Si, K, Zn, Ca, Co, Mg, Be, V, Se, Fe, Cu, As, Pb, Mo, Ag, Sb, Cd, Cr	Al, Si, K, Zn, Ca, Co, Mg, Be, V, Se, Fe, Cu, As, Pb, Mo, Ag, Sb, Cr

<u>Where:</u>
Group I: risk potential /1000 > 10 000
Group II: risk potential factor/1000 = 10-1000
Group III: risk potential facor/1000 = 1-10
Group IV: risk potential factor/1000 <1

<u>Assumptions:</u>

- Only elements in the SCE residual silicate fraction are inert or "non-reactive" in the oxidation zone over the long-term
- Attenuation of elements as a result of secondary ppt and adsorption is assumed to be in accordance with the values derived from the thermodynamic predictions in Table 3.13, Section 3.2
- Only elements in the SCE water-soluble, exchangeable and carbonate fractions are likely to react with acidic pore waters in the unoxidised impoundment zones

<u>Acid generating potential</u>

The results of the Acid Base Accounting (ABA) are summarised in Table 3.29.

Table 3.29: Acid Base Accounting test results – porphyry-type copper sulphide tailings sample

Parameter	Standard Sobek method	Modified single H_2O_2 addition method	Modified H_2O_2 incremental addition method
Maximum acid production potential (AP, MPA or APP): kg/t H_2SO_4	89		
maximum acid neutralisation potential (NP) or capacity (ANC): kg/t H_2SO_4	66	28	26
Net Acid Producing Potential (NAPP)	23	61	63
Net Neutralisation Potential (NNP)	-23	-61	-63
Net Potential Ratio (NPR)	0.74	0.32	0.29
Classification	Acid generating	Acid generating	Acid generating

These results confirm that the standard Sobek method overestimates the acid neutralising potential of the sulphide tailings, due to incomplete oxidation of Fe(II) formed through the dissolution of siderite and/or pyrite oxidation. The results from the two tests involving the addition of H_2O_2 indicate that the mode of addition (single dose or incrementally) does not have a significant effect on ANC

The results of the Net Acid Generating (NAG) tests are summarised in Table 3.30.

Table 3.30: NAG test results– porphyry-type copper sulphide tailings sample

Parameter	Single NAG	Sequential NAG	Kinetic NAG
NAG_{pH}	2.6	2.6	
NAG at pH 4.5: kg/t H_2SO_4	10.8	22.7	
NAG at pH 7: kg/t H_2SO_4	15.1	39.6	
Time to temperature peak and pH stabilisation			354 minutes
Classification	Highly acid generating	Highly acid generating	Slow kinetics with gradual decline in pH over time.

The results in Table 3.30 confirm reports in the literature i.e. that the single NAG test underestimates the acid generating potential due to incomplete oxidative dissolution of pyrite. Nevertheless, as in the case of the ABA tests, both the single and sequential NAG tests indicate that the sample is “highly acid generating”. The kinetic NAG test indicates that the generation of acid will , however, be relatively slow - corresponding to a potentially gradual decrease in the pore water pH in the oxidation zone over time. The rate of change in temperature and pH during the kinetic NAG test is illustrated in Figure 3.11.

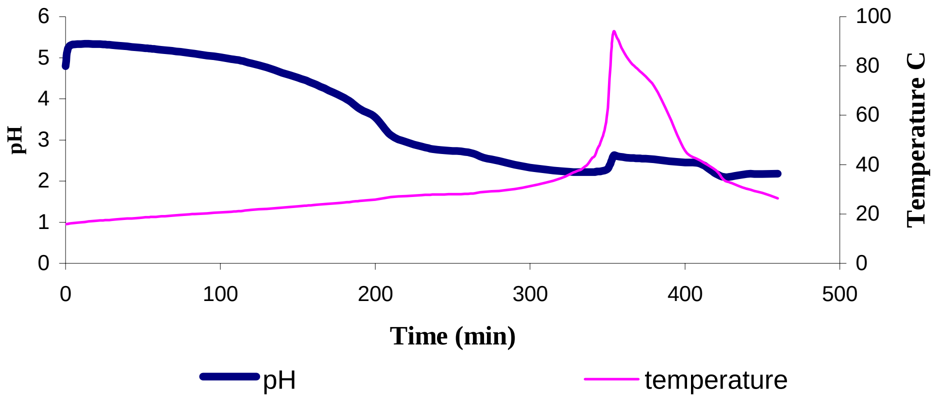


Figure 3.11: Kinetic NAG profile for the porphyry-type copper sulphide tailings sample

3.4 Quantitative Assessment of the Potential Environmental Impacts Associated with a Specific Porphyry-Type Copper Sulphide Tailings Sample

The final task on this case study entails quantitative predictive modelling of the time-related generation and dispersion of contaminated leachate from a porphyry-type copper sulphide tailings wastestream in a hypothetical disposal scenario, and the subsequent derivation of an associated impacted land footprint indicator for decision-support purposes.

Before this can be achieved, it is necessary to “tailor” the generic leachate generation model structure, described within Section 2.4.1 of the report, so as to incorporate the reaction mechanisms and parameters of particular relevance to this waste type. This section thus begins with a description of a leachate generation model specific to copper sulphide tailings wastes (Section 3.4.1). Section 3.4.2 subsequently demonstrates how this model can be used - in conjunction with waste characterisation and management data, as well as the fate and transport models and impact quantification methodologies developed within Chapter 2 - to quantify the water-related impacts associated with the porphyry-type copper sulphide tailings waste described in the previous section.

3.4.1 Development of a leachate generation model for copper sulphide tailings

Section 2.4.1 developed a generic model structure which takes into account the non-ideal flow conditions and oxygen diffusion mechanisms in both saturated and unsaturated disposal regimes. This sub-section expands this hydrodynamic and oxygen diffusion model framework, to include the chemical reaction mechanisms characteristic of copper sulphide tailings, with special attention paid to sulphide mineral oxidation.

Chemical reaction model equations

The purpose of modelling is to simplify reality so that the prediction of leachate generation behaviour and ultimate environmental impact is possible. Simplification is necessary given the limitations not only of current understanding of reaction mechanisms and species interactions, but also computational capacity. As such, the model presented here only includes those reactions and processes considered most important, viz: sulphide mineral oxidation through a modified shrinking core approach; abiotic and biotic ferrous ion oxidation reactions; carbonate and silicate mineral dissolution; and secondary precipitation and adsorption equilibrium reactions:

- *Kinetically-controlled sulphide mineral oxidation reactions*

As discussed in Section 3.1 of this chapter, acid mine drainage is caused by exposure of sulphide-containing mined materials (often pyrite) to oxygen and water which results in the oxidation of pyrite to ferric sulphate. The aqueous oxidation of pyrite is a heterogeneous surface-controlled process that occurs through a complex series of reactions that includes chemical, biological and electrochemical mechanisms. Both oxygen and ferric iron are the oxidants of pyrite. At low pH, oxidation of pyrite by Fe^{3+} is the main mechanism for acid production, since this reaction is much faster than the oxidation of pyrite by oxygen and the presence of bacteria accelerates the oxidation of ferrous to ferric iron significantly. Thus it is generally accepted that the oxidation of pyrite occurs predominantly by ferric iron at low to circumneutral pH and the role of dissolved oxygen is to oxidise ferrous to ferric iron and perpetuate the cycle of pyrite oxidation by ferric iron. Chalcopyrite ($CuFeS_2$) is oxidised in much the same way as pyrite. The overall stoichiometry of pyrite and chalcopyrite oxidation is described by reactions in Equations 3.1-3.4 and Equations 3.3-3.6 respectively.

$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$	Equation 3.1
$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$	Equation 3.2
$Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O$	Equation 3.3
$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_{3(s)} + 3H^+$	Equation 3.4
$CuFeS_2 + 4O_2 \rightarrow Fe^{2+} + Cu^{2+} + 2SO_4^{2-}$	Equation 3.5
$CuFeS_2 + 16Fe^{3+} + 8H_2O \rightarrow 17Fe^{2+} + Cu^{2+} + 2SO_4^{2-} + 16H^+$	Equation 3.6

A number of models have been developed specifically for simulating oxidation of pyrite-containing wastes. A characteristic feature of these models (namely Davis & Ritchie, 1986; Gerke et al., 1998; and Wunderly et al., 1996) is that they assume that oxygen diffusion to the reaction site is rate limiting, and employ shrinking core model kinetics to describe the oxidation of pyrite. This approach represents the current level of sophistication in the field of pyrite oxidation modelling (Gerke et al., 1998) and is attractive due to its simplicity. The shrinking core approach is, however, not without its shortcomings. The first of these is that reaction product stoichiometry is determined by bulk phase conditions (through the local equilibrium assumption and iron speciation considerations), which are likely to be very different from solution conditions at the reaction site. Another aspect relates to ferrous ion oxidation. As a consequence of the difficulties surrounding reaction product stoichiometry, ferrous ion oxidation is not modelled explicitly in the shrinking core model. In fact, ferrous ion oxidation is assumed to occur instantaneously at the reaction front and its regeneration is assumed to be instantaneous. There is thus no consideration of ferrous ion oxidation kinetics and the role of bacteria in accelerating oxidation.

The work by Hansen (2004) addresses these limitations, by including kinetic terms to account for both abiotic and biotic ferrous ion oxidation, and by separating pyrite oxidation by oxygen and pyrite oxidation by ferric ion. Figure 3.12 depicts the conceptual modelling approach to sulphide oxidation from unsaturated and saturated copper sulphide tailings.

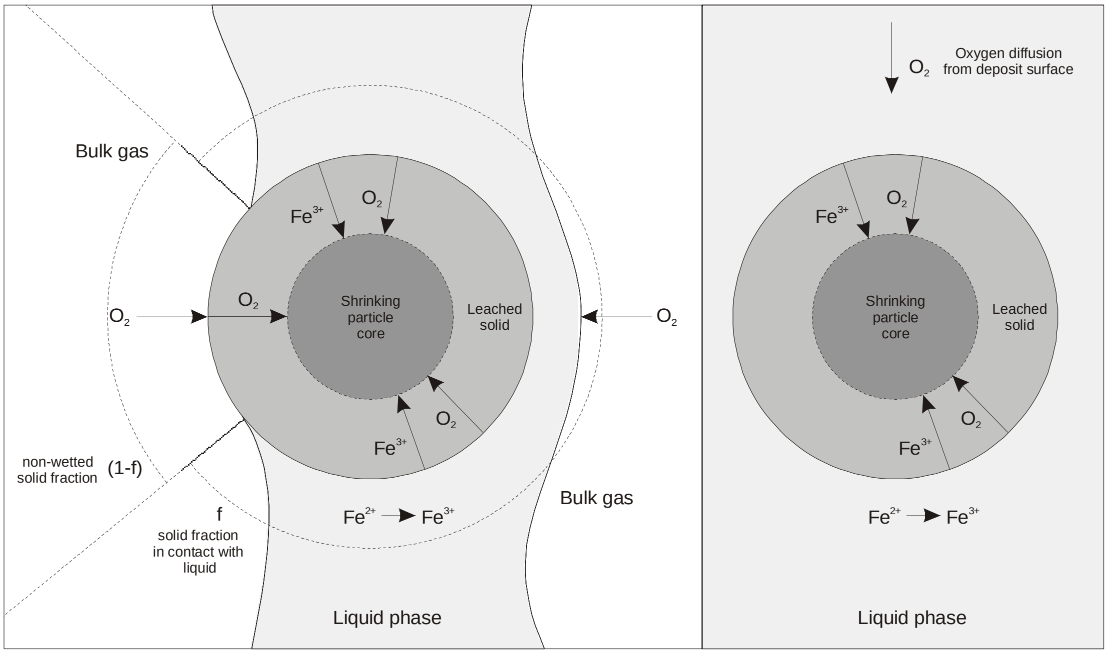


Figure 3.12: Conceptual diagram of functional modelling approach for sulphide mineral oxidation in unsaturated and saturated tailings showing significant phases and processes

Here, the hydrodynamic flow behaviour is represented as before. Oxygen diffuses from the bulk gas phase into the liquid phase and directly into the fully-wetted particle pores from the non-wetted surface fraction. In the liquid phases, dissolved oxygen either oxidises ferrous ion to ferric ion or diffuses into the particle pores to oxidise pyrite and chalcopyrite directly. It is assumed that ferric ions also diffuse into the particle pores and oxidise pyrite and chalcopyrite and that this may be represented by shrinking core model kinetics. The derivation of the modified shrinking core model equations for sulphide oxidation is detailed in Appendix J.

- *Kinetically-controlled ferrous ion oxidation*

As discussed above, the model developed by Hansen includes kinetic terms to account for both abiotic and biotic ferrous ion oxidation, presented in Table 3.31.

Table 3.31: Rate expressions describing ferrous iron oxidation to ferric iron

Reference	Rate expression	Rate constant	Notes
Stumm & Morgan (1981)	$k[Fe^{2+}][O_2][H^+]^{-2}$	$k = 10^{-8.22}$ mol.m^{-3}.s^{-1}	- volumetric rate of ferrous iron oxidation - abiotic - valid up to pH 7
Kirby et al. (1999); Pesic et al. (1989)	$k.C_{bact}[Fe^{2+}][O_2][H^+]$	$k = 10^{-10.29}$ m^9.mg^{-1}.mol^{-2}.s^{-1}	- volumetric rate of ferrous iron oxidation - biotic - valid up to pH 3 - below pH 2.2 rate is independent of $[H^+]$ - Concentrations in mol.m^{-3} except C_{bact} which is the concentration of *Thiobacillus ferrooxidans* in mg.m^{-3} dry weight

* All concentrations as mol.m^{-3}

To avoid model discontinuities and the ensuing computational effort that result from the above rate expressions, a continuous rate function was developed by summing the pH dependent biotic rate of Kirby *et al.* (1999) and the pH dependent abiotic rate of Stumm & Morgan (1981).

The reaction term for ferrous ion oxidation in the liquid phase continuity equations is then given by:

$$\sum R = \theta_l(s_{i,abiotic}k_{abiotic}\frac{C_{Fe^{2+}}C_{O_2}}{(C_{H^+})^2} + s_{i,biotic}k_{biotic}C_{Fe^{2+}}C_{O_2}C_{H^+}C_{bact})$$

Where s_i is the stoichiometric coefficient for the particular species and reaction and k is the rate constant as given in Table 3.31.

- *Kinetically-controlled carbonate mineral dissolution kinetics*

Although carbonate can be present in sulphide tailings in the form of calcite, dolomite, ankerite and/or siderite, calcite is generally considered to be the predominant carbonate mineral. The model case here included acid hydrolysis reactions for both calcite and dolomite, as represented by Equations 3.7-3.8 and 3.9-3.10 respectively:

pH< 6: $CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2CO_3$	Equation 3.7
6.5 < pH < 10: $CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$	Equation 3.8
pH< 6: $CaMg(CO_3)_2 + 4H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2H_2CO_3$	Equation 3.9
6.5 < pH < 10: $CaMg(CO_3)_2 + 2H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$	Equation 3.10

The kinetic mineral dissolution and precipitation rate law described by Lasaga (1984) and Steefel & Lasaga (1994) is used in the copper tailings model:

$$r_m = A_m k_m \left[1 - \left(\frac{IP_m}{K_m}\right)^{\mu}\right]^n .$$

where m is the mineral index, r_m is the dissolution or precipitation rate, A_m is the specific reactive surface area [$m^2.kg^{-1}H_2O$], k_m is the rate constant [$mol.m^{-2}.s^{-1}$] which may be temperature dependent, K_m is the equilibrium constant for the mineral-water reaction written for the destruction of one mole of mineral m, and IP_m is the ion activity product. The parameters μ and n are taken equal to unity. A particular advantage of this approach is that the above rate expression applies to both supersaturated and undersaturated conditions and the rate approaches zero as conditions approach equilibrium (i.e. IP_m/K_m tends to 1 at equilibrium).

The temperature dependence of the rate constant is given by the following equation:

$$k = k_{25} \exp\left[\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right].$$

where E_a is the activation energy, k_{25} is the rate constant at 25°C, R is the gas constant, T is absolute temperature. Determining the reactive surface area is complex as the mineral surface changes with time.

Often the surface area is related to the mineral volume fraction so that:

$$A_m = A_m{}^0 \frac{V_f}{V_f{}^0}.$$

where A_m and V_f are the reactive surface area and volume fraction of the mineral respectively and the superscript 0 indicates initial values at time t = 0. Characterising the initial specific reactive surface area, $A_m{}^0$ is still difficult and so the values used in this study were set at $10cm^2.g^{-1}$. This is consistent with values reported in Audigane et al. (2006) and Gaus et al. (2006).

Relevant kinetic constants are given in Table 3.32.

Table 3.32: Rate expressions describing carbonate dissolution reactions (from Linklater et al., 2005)

Reaction	k_{25}	Activation Energy, E_a	Reference
Calcite dissolution	1.60×10^{-9} mol.m^{-2}.s^{-1}	41.87 kJ.mol^{-1}	Svensson & Dreybrodt (1992)
Dolomite dissolution	0.60×10^{-9} mol.m^{-2}.s^{-1}	41.87 kJ.mol^{-1}	assigned based on calcite

- *Kinetically-controlled silicate mineral dissolution*

The model case developed here included dissolution of quartz, K-feldspar and muscovite, as represented by Equations 3.11-3.13 respectively:

Quartz dissolution: $SiO_2 + 2H_2O \rightarrow H_4SiO_4$	Equation 3.11
K-feldspar dissolution: $KAlSi_3O_8 + 4H_2O + 4H^+ \rightarrow K^+ + Al^{3+} + 3H_4SiO_4$	Equation 3.12
Muscovite dissolution: $KAl_2[AlSi_3O_{10}](OH)_2 + 10H^+ \rightarrow K^+ + 3Al^{3+} + 3H_4SiO_4$	Equation 3.13

Silicate minerals can be described using the rate law of Lasaga (1984). Relevant rate constants are provided in Table 3.33.

Table 3.33: Rate expressions describing silicate dissolution reactions (from Linklater et al., 2005; Brookfield et al., 2006)

Reaction	Rate expression	Rate constant	Notes
Quartz dissolution	$k.A_q[1\text{-}IP_q/K_q]$	$k = 5 \times 10^{-7}$ mol.m^{-2}.s^{-1}	- A_q is the reactive surface area of quartz
K-feldspar dissolution	$k.A_{kf}$	$k = 4.1 \times 10^{-13}$ mol.m^{-2}.s^{-1}	- A_{kf} is the reactive surface area of k-feldspar
Muscovite dissolution	$A_{mu}(k_1[H^+]^{0.4} + k_2)$	$k_1 = 9.5 \times 10^{-15}$ mol$^{0.6}$.m$^{1.2}$.m^{-2}.s^{-1} $k_2 = 1.8 \times 10^{-15}$ mol.m^{-2}.s^{-1}	- A_{mu} is the reactive surface area of muscovite
All concentrations as mol.m^{-3} Reactive surface area of mineral [m^2.m^{-3} of media] is calculated based on the premise that each mineral contributes to the total reactive surface area of the material in an amount proportional to its volume abundance in the material.			

- *Equilibrium-controlled reactions*

A number of secondary precipitation reactions, as well as adsorption of anions and cations by secondary ferrihydrite, are incorporated into the leachate generation model framework by interfacing the model with a proven solution speciation thermodynamic model, such as MINTEQA2 (see discussions in the following section). Those secondary precipitation reactions considered to be of key significance to this specific case study, are represented by Equations 3.14 -3.23.

Ferrihydrite precipitation*:* $Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+$	Equation 3.14
Goethite precipitation*:* $Fe^{3+} + 2\ H_2O \leftrightarrow \alpha\text{-}FeOOH + 3H^+$	Equation 3.15
Schwertmannite precipitation: $8Fe^{3+} + SO_4^{2-} + 14H_2O \leftrightarrow Fe_8O_8(OH)_6(SO_4) + 22H^+$	Equation 3.16
Jarosite precipitation: $3Fe^{3+} + K^+ + 2SO_4^{2-} + 6H_2O \leftrightarrow KFe_3(OH)_6(SO_4)_2 + 6H^+$	Equation 3.17
Gypsum precipitation: $Ca^{2+} + SO_4^{2-} + 2H_2O \leftrightarrow CaSO_4.2H_2O$	Equation 3.18
Kaolinite precipitation: $2Al^{3+} + 2H_4SiO_4 + H_2O \leftrightarrow Al_2Si_2O_5(OH)_4 + 6H^+$	Equation 3.19
Gibbsite precipitation*:* $Al^{3+} + 2H_2O \leftrightarrow AlOOH + 3H^+$	Equation 3.20
Alunite precipitation: $3Al^{3+} + K^+ + 2SO_4^{2-} + 6H_2O \leftrightarrow KAl_3(OH)_6(SO_4)_2 + 6H^+$	Equation 3.21
Jurbanite precipitation: $Al^{3+} + SO_4^{2-} + H_2O \leftrightarrow Al(OH)SO_4 + H^+$	Equation 3.22
Amorphous silica precipitation: $H_4SiO_4 \leftrightarrow SiO_2\,(am) + 2H_2O$	Equation 3.23

The model algorithm and solution technique

The leachate generation model developed here is coded up in the gPROMS (PSE, 2002) environment. gPROMS is a general purpose modelling, simulation and optimisation tool, and was chosen to implement the leachate generation model equations for a number of reasons. Firstly, gPROMS allows modelling of discontinuous processes. Discontinuities will be present in the physical and chemical behaviour displayed by leachate generation systems. Secondly, gPROMS is well suited to distributed systems. Again, this is a feature of leachate generation systems, where properties vary in one or more spatial dimensions as well as time. Finally, gPROMS is extremely flexible as it allows the direct mathematical description of distributed systems. This means that the modeller can avoid becoming involved in the complex mathematical manipulations of the model equations to obtain a solution. Crude approximations, such as the CSTRs in series approach, are also avoided. This final characteristic of gPROMS is particularly advantageous in terms of the stated model requirements. A model coded up in gPROMS will be transparent in that the model equations are evident and able to be amended if necessary. The only drawback of using gPROMs in this context is the lack of the control over the time step. This means that equilibrium reactions cannot be included in the model through the simple calculation of a pseudo rate term. An alternative for incorporating equilibrium reactions into the gPROMS model framework, which is the approach taken here, is to interface a proven solution speciation model such as MINTEQA2 (Allison et al., 1991) into the gPROMS model.

3.4.2 Predictive modelling and impact quantification

In this sub-section of the report, the copper sulphide tailings leachate generation model is used to predict the concentrations of mobile contaminants for a number of waste management scenarios at the interface between the deposit and the environment. Further modelling of subsequent groundwater flow and mass transport followed by impact assessment serves to demonstrate the quantitative approach to predicting potential environmental impact for the scenarios.

Scenario description

To demonstrate the model capabilities and the overall approach to quantitative assessment of solid waste impacts a simple case study, which compares saturated and unsaturated tailings deposits, is considered here. This case study serves to investigate the effect of tailings saturation on subsequent leachate generation; contaminant mobility; and resulting potential environmental impact. The effect of adding a cover is also investigated. In this case study we assume a fixed amount of copper tailings waste in each of the deposit scenarios of 100 kt.

The first scenario is an unsaturated tailings deposit. For the tailings to be unsaturated throughout most of their depth, a deposit height of 2m is selected. In reality, tailings deposits range in height from 5m to 30m. This scenario therefore represents an extreme situation as it is likely that most of the sulphide minerals will be oxidised during the life of the deposit. The second scenario is a saturated deposit, where oxygen ingress is through diffusion from the top of the deposit in the liquid phase. A deposit height of 10m is selected, which results in a smaller deposit area as the deposit capacity remains the same. The final scenario considers a 10m saturated tailings deposit which has been covered to reduce the hydraulic conductivity and thus reducing both oxygen ingress and water ingress further. The relevant scenario parameters, in terms of the variables investigated in this study, are given in Table 3.34 below. Detailed model input parameters are presented in Appendix K1.

Table 3.34: Model case study scenario parameters

Scenario	Hydraulic conductivity [$m.s^{-1}$]	Saturation factor	Deposit height [m]	Deposit area [m^2]
Unsaturated deposit	1×10^{-6}	0.5	2	32260
Saturated deposit	1×10^{-6}	1	10	6450
Saturated deposit covered	1×10^{-8}	1	10	6450

Leachate generation modelling results

The leachate generation model predicts the time dependent leachate concentrations throughout the deposit, as well as the amounts of sulphide and other minerals remaining after each time step. The results of the unsaturated scenario demonstrate the model capabilities most effectively as sulphide oxidation proceeds rapidly and throughout the depth. The limited diffusion of oxygen in the saturated scenarios means that sulphide oxidation proceeds slowly and is limited to the very top of the deposit. Figure 3.13 shows the depth profiles of gas phase oxygen content and sulphide conversion for the unsaturated deposit. These figures serve to demonstrate the scale of the sulphide oxidation problem: even after 100 years, oxygen (and the associated reaction front) has only penetrated to a depth of

1.5m. This has implications for tailings management as it is unlikely that long term stability of tailings deposits can be assured post closure. In light of this, an alternative management approach may be to accelerate sulphide oxidation and manage the resulting liquid effluent over the life of the operation. The figures below suggest that the deposit should be sparged with air, similarly to heap leach operations, at intervals of approximately 0.5m if this approach is to be adopted.

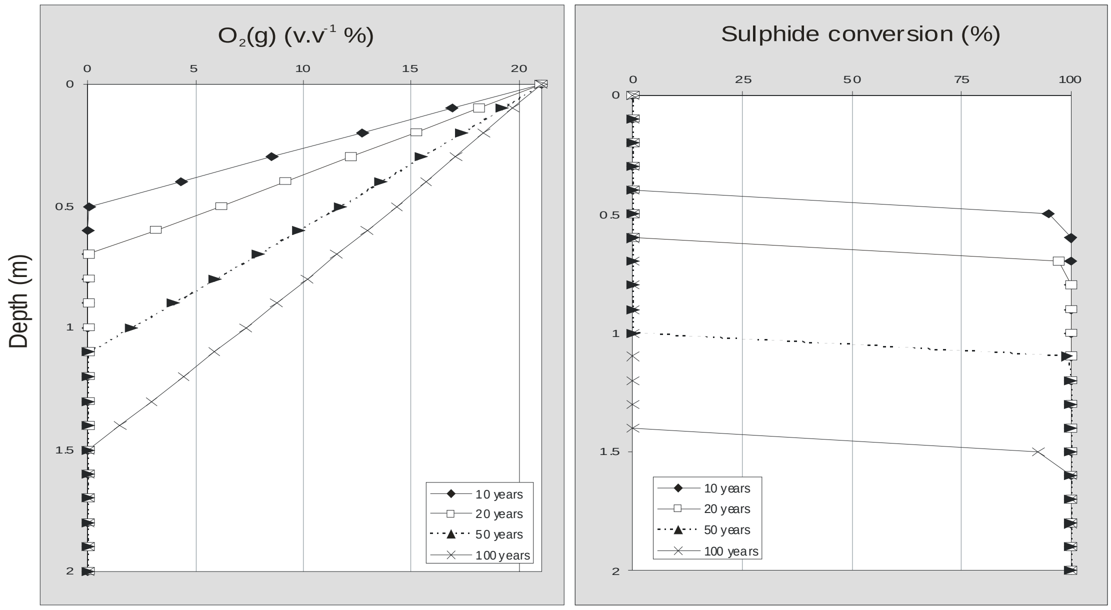


Figure 3.13: Bulk gas phase oxygen content and sulphide conversion as a function of depth for the unsaturated scenario

Figure 3.14 shows the corresponding pH, sulphate and ferrous iron leach profiles at the base of the unsaturated (or oxidised) deposit zone.

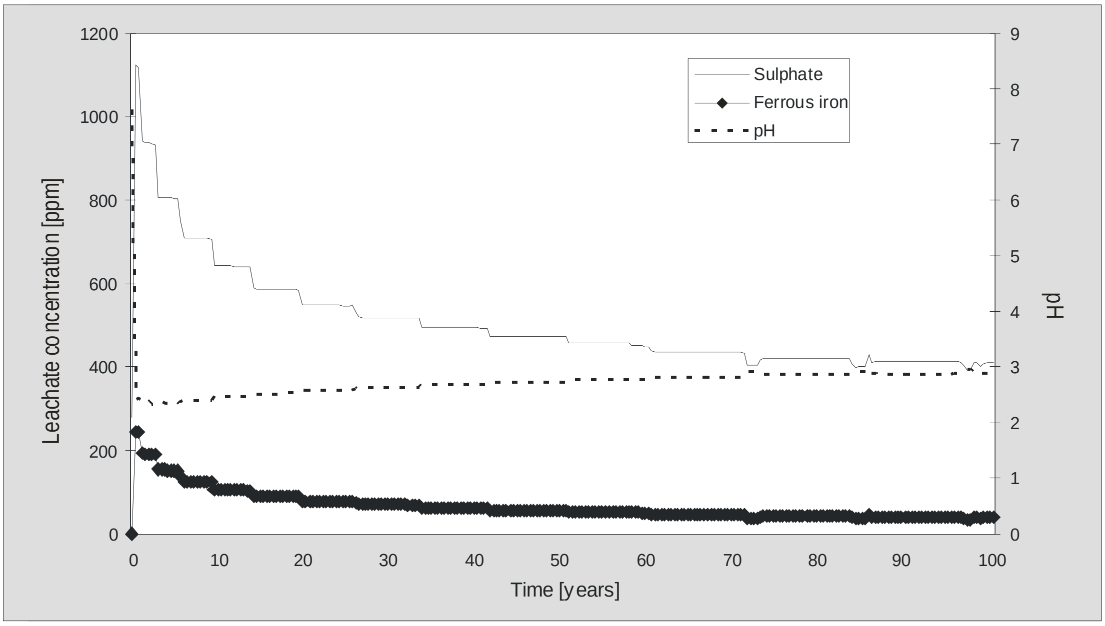


Figure 3.14: Time-dependent pH and leachate concentration profiles for sulphate and ferrous iron at the base of the unsaturated deposit scenario

Average leachate generation modelling results for all the scenarios are presented in Table 3.35.

Table 3.35: Averaged results from leachate generation modelling for unsaturated and saturated scenarios

Scenario	Average pH	Sulphate (ppm)	Fe (ppm)
Unsaturated deposit	2.7	504	65
Saturated deposit	7.0	297	5
Saturated deposit covered	7.6	280	0

Table 3.36 compares the unsaturated model results with the literature values presented in Appendix E3 and indicates that both the sulphate and iron values predicted by the model are lower than the reported values for generic copper and other base metal sulphide tailings impoundments.. These discrepancies can be attributed to the relatively low sulphide sulphur content in the modelled porphyry-type copper sulphide tailings sample (4.4%) in comparison with the tailings deposits reported in the literature (> 10% sulphur). However, the predicted pH is within the range suggested in the literature for surface and oxidised zones of tailings impoundments, and is consistent with the predicted high acid generating/low neutralising capacity of the tailings sample (see Section 3.3.3).

Another possible explanation for the discrepancies between predicted results and literature values could be the simplified hydrodynamics and estimated waste management parameters employed in the model. Ideally, the model should be calibrated with field data and better estimates obtained for some of the parameters related to waste management. Provisional model runs, also shown in Table 3.3.6, with reduced liquid flowrates (in line with South African rainfall figures) together with sulphide and carbonate contents in the region of the literature values yielded sulphate and iron levels within the range observed in the literature. This gives confidence in the leachate generation model’s ability to accurately predict sulphide oxidation from tailings-type waste deposits.

Table 3.36: Comparison of modelled results with literature values

	Literature (oxidation zone)	Modelled (unsaturated)	Revised model (low flow)	Revised model (high S, Ca, low flow)
pH	2.3 – 4.4	2.7	1.3	3.5
Sulphate (ppm)	1000 – 50 000	504	6600	15 000
Fe (ppm)	80 – 8000	65	1800	4000

Groundwater flow and mass transport modelling

Only selected results from the leachate generation model are used to determine the fate and transport of contaminants and the resulting impacted land footprint. These are: the ionic strength of the leachate, as a measure of salinity, and the concentration of ferrous iron, as the selected strategic metal. Iron is selected as a strategic metal for sulphide containing wastes, such as the porphyry-type copper sulphide tailings under investigation here, as it is a product of sulphide oxidation. Furthermore, qualitative characterisation of generic base metal sulphide tailings impoundments has indicated that iron is a potentially significant element in terms of environmental impact (see Tables 3.14 and 3.15 in Section 3.2). Although iron has not been linked to significant health impacts (insofar as there is insufficient data to set a guideline value based on health considerations), it has adverse aesthetic and taste effects.

The groundwater flow and transport model chosen to support the generation of footprint indicators defaults to generic hydrogeological data inputs, representative of a sandy aquifer type, and makes a number of simplifying assumptions. These assumptions are justified as the role of the impact prediction modelling in this case is not to quantify absolute impact, but to give an indication of relative impact arising from tailings management between the possible scenarios in order to demonstrate the impact assessment methodology. Furthermore, it can be assumed that the disposal sites would be identical, and so there is little to be gained from a site-specific assessment, even if this data were available.

Model input data and assumptions are detailed in Appendix K2.

Impacted land footprint generation

The results of the footprint analysis are summarised in Table 3.37. Here, the boundary of impacted land for salinity and iron (the strategic metal) is based on water quality guidelines. To delineate salinity footprints an ionic strength of 0.015 based on a salinity guideline for TDS of 1000 mg.l^{-1} has been used, whilst an iron concentration of 0.3 mg.l^{-1} is used to determine the metals footprints. These guideline values are taken from the ANZECC water quality guideline values for domestic use (ANZECC1999). South African domestic use guidelines are more stringent with values of 450 mg.l^{-1} for TDS and 0.1 mg.l^{-1} for iron (DWAF, 1996), while ANZECC further quote a guideline value for iron of 10 ppb to ensure protection of aquatic ecosystems. Using these values would result in even larger footprints than those presented in Table 3.37, although the relationship is not directly proportional. Hansen (2004) presents a parametric analysis which investigates the effect of changing parameters, such as guideline values and aquifer properties, on the resulting footprints. Further study shows that a twenty fold decrease in guideline value results in only a five fold increase in footprint size.

Table 3.37: Impacted land footprint indicator results for the various waste management scenarios

	Unsaturated deposit	Saturated deposit	Saturated deposit covered
Metals Impacted land footprint (km^2.years)	34 500	220	-
Characteristic parameters:			
Maximum footprint (m^2)	6 712 000	295 000	
Time when maximum occurs (years)	21 053	1699	
Variance (years^2)	101 981 000	1 377 000	
Salinity Impacted land footprint (km^2.years)	437	3	-
Characteristic parameters:			
Maximum footprint (m^2)	337 000	46 000	
Time when maximum occurs (years)	771	34	
Variance (years^2)	3 462 000	12 700	

As anticipated, the unsaturated deposit gives rise to the largest metals and salinity impacted land footprints. This is a function of the higher leachate concentrations together with the larger deposit area. There was no discernable salinity or iron footprint for the saturated and covered deposit as a result of the reduced flowrate through the deposit and negligible sulphide oxidation. Viewing the characteristic footprint parameters in Table 3.37 also gives an indication of the extent of the resulting pollution plumes and their prolonged nature. A comparison of the results in Table 3.37 with the area of the modelled deposit (see Table 3.34) indicates that for salinity, the maximum footprints are about an order of magnitude larger than the deposit area. For metals the maximum footprints are approximately two orders of magnitude larger.

CHAPTER 4: CONCLUSIONS AND RECOMMENDATIONS

This research project has developed and demonstrated a methodology for the quantitative prediction of water-related environmental impacts associated with solid mineral wastes that addresses the deficiencies and limitations of current approaches. In addition, this approach extends the current capabilities of the primary resource-based industries to assess, manage and improve their environmental performance and, ultimately, meet their sustainability objectives.

The methodology developed here effectively couples waste characterisation studies and rigorous leachate generation modelling with fate and transport modelling to obtain an impacted land footprint indicator – a measure of the degree to which a land mass is impacted by leachate generation from solid waste deposits.

This chapter presents the key findings of the project (Section 4.1); identifies further research and development requirements (Section 4.2); and, finally, highlights the significance of the approach in terms of future application (Section 4.3).

4.1 Summary of Key Project Findings and Outcomes

This section presents a discussion summarising the main issues and problems underpinning this study (Section 4.1.1); the key aspects of the proposed approach for addressing these issues (Section 4.1.2); as well as the main observations arising from the case study applications (Section 4.1.3).

4.1.1 The need for a new approach to environmental impact assessment of solid waste management for the primary industries

Chapter 1 of the report highlighted the current situation pertaining to solid wastes from the primary mineral-based resource industries, thus providing the necessary motivation for the development of a new approach to address the identified shortcomings. In summary, the proposed approach for the prediction of solid mineral waste impacts developed from the recognition of the following key issues:

1. Solid wastes pose a particular problem for the primary industries, which produce vast tonnages of solid waste annually, and whose overall environmental performance is largely a function of the success or failure of waste management strategies to minimise long-term liability.
2. In order to be effectively managed, potential impacts and risks associated with solid mineral wastes first need to be quantitatively predicted. Furthermore, in a legislative framework leaning towards preventative rather than remedial approaches, it is equally important that the quantification of environmental impacts and liabilities be brought into the early design stages of the project life cycle, where the choice of appropriate technology can effect a reduction in both the amounts of waste generated and the environmental hazards associated with the wastes.
3. That said, solid wastes present a number of unique challenges to impact assessment. This is because solid mineral wastes are generally comprised of a multitude of components – the mobility of which is governed by a large number of inter-related mechanisms and parameters. Furthermore, the impact is not associated with the quantity of waste generated *per se* but rather with the generation of leachate, the subsequent migration of contaminants into the environment and their bioavailability. Difficulties also arise because solid waste impacts are protracted and there is a significant time lag between the generation of the waste by the process and the manifestation of adverse environmental effects. Leachate generation processes are also time-dependent and the resulting environmental concentrations are spatially distributed. The relationship between solid

waste generation and resulting impact is therefore decidedly nonlinear and a function of a multitude of process-specific, waste-specific and site-specific factors.

4. Overcoming these challenges is difficult as wastes are generally poorly characterised, and the mechanisms of leachate generation not well understood. Furthermore, current impact assessment tools are deficient in their ability to capture the environmental impact of solid wastes. The focus is either too much on the waste, in that the volume or mass of waste is recorded as an indicator of impact, or too much on latter steps in the causal mechanism chain from interventions to endpoints. The level of uncertainty and abstraction in obtaining these types of indicators brings into question their applicability and relevance especially to the generators of the wastes –including the primary industries. In particular, no direction is given on ways to reduce impact as there is no sensitivity to process variables, waste management strategies or other site- and process-specific factors.

The motivation for developing a new approach was thus two-fold: to address the deficiencies of current solid waste impact assessment methods; and also to provide tools which are of value to the primary industries in their ongoing efforts to improve their environmental performance and meet sustainability objectives.

4.1.2 The proposed methodology for the quantitative prediction of solid mineral waste environmental impacts

In line with the overarching objective and specific aims of this research project, Chapter 1 proposed a conceptual approach for the stepwise prediction of the environmental impacts associated with solid wastes from the primary mineral-based industries. Chapter 2 of the report was subsequently aimed at developing the understanding, protocols and scientific techniques underpinning each methodological step in the proposed approach, namely: problem formulation (step 1), qualitative waste characterisation (step 2), quantitative waste characterisation (step 3), leachate generation modelling (step 4), fate and transport modelling (step 5); and, finally, quantification of the environmental impact (step 6). This sub-section of the report highlights some of the key features of the proposed approach and supporting tools.

A key feature of the proposed approach is that it focuses on, and is largely underpinned by a fundamental understanding of, each step in the causal mechanism chain, namely: ore formation → ore extraction & beneficiation → waste disposal → leachate generation → leachate dispersion → environmental impact. As such, the methodology is able to quantify the complex interrelations between the ore deposit; the processes generating the waste; the waste deposit and its management; and the resulting environmental impact. This focus on the waste, its characteristics (influenced by upstream processes) and its leach behaviour (influenced by waste management and site-specific factors), makes a significant advance in terms of current impact prediction methodologies.

The quantification of both the inherent spatial and temporal nature of the environmental impact through rigorous modelling of emissions and transport in the environment, is considered an essential feature of the proposed approach, and represents yet another significant contribution to current impact assessment methods. Together, the leachate generation and contaminant dispersion models provide a measure of the rate and extent of the groundwater contaminant plume associated with a solid waste disposal site, and thus represents essential steps in the risk-based assessment of their environmental impact. However, the proposed methodology makes a clear distinction between leachate generation and its subsequent subsurface transport, and the two are decoupled despite the fact that they have many processes in common and can thus be modelled similarly.

This decoupling is considered necessary as leachate generation is a direct function of waste generation and management practices. The identification of opportunities to reduce environmental impacts through process design and operational improvements thus requires accurate and reliable prediction of the generation of contaminated leachate as a function of these key influencing factors. Section 2.4 of the report thus concerned itself with the development of a rigorous mechanistic leachate generation model to specifically describe leachate generation from solid waste deposits under non-ideal flow conditions. This was necessary as the development of mechanistic leachate generation models has been typically limited, and those which have been developed are either too simplistic or too abstract. The generic leachate generation model developed here focuses on improving the hydrodynamic representation and incorporating oxygen transport – a critical rate-controlling process for pyrite-containing wastes from the primary industries. Section 2.4 of the report also proposed a conceptual approach for systematically tailoring the generic model structure to specific wastes by including the waste properties and processes that are significant for certain types of waste outputs.

In this regard, the proposed methodology recognises waste characterisation as an important step in the development of the leachate generation model and, ultimately, prediction of the impacts arising from the land disposal of a solid mineral waste. Conventional waste characterisation methodologies, which are typically based on criteria such as chemical compositions, physical properties and leach behaviour, can only provide a partial picture of the time-dependant leachate generation potential. Nevertheless rigorous waste characterisation plays a vital and integral part of leachate generation predictions in terms of identifying the strategic contaminants and controlling leach mechanisms, and in the generation of quantitative data to describe such mechanisms. Although a large number of methodologies have been developed for the characterisation of solid wastes, the objective behind waste characterisation is frequently merely to classify or type the wastes, rather than to provide a better understanding of the complex and time-dependant behaviour within a deposit. Section 2.3 of the report thus concerned itself with the development of a generic protocol, whereby solid mineral waste characterisation is conducted in a number of systematic stages corresponding to various levels in terms of accuracy and detail of the derived data. A significant feature of this protocol is the use of qualitative waste characterisation (level 1 studies) to guide and inform the subsequent execution of quantitative waste characterisation techniques–which include empirical analysis of physio-chemical properties (level 2 studies), as well as empirical tests and thermodynamic modelling to assess the leach behaviour of selected contaminants (level 3-5 studies).

In the methodology proposed here, qualitative waste characterisation essentially serves as a screening assessment and has two specific purposes, namely: 1) to predict likely physio-chemical properties of wastes on the basis of the feed ore characteristics (i.e. waste origins) and generating processes (i.e. waste source); and 2) to subsequently predict strategic constituents of potential environmental significance on the basis of criteria relating to hazard potential and mobility in a disposal scenario. A structured and generalised strategy for predicting key environmental characteristics of solid mineral wastes, on the basis of their origins and source has thus been developed in Section 2.2 of the report. A key feature of the qualitative waste characterisation methodology developed here is the reconciliation of available empirical data with a fundamental understanding of the mechanisms and parameters influencing element distribution behaviour and properties during ore formation, ore extraction & beneficiation, and, finally, waste disposal. This hybrid type of semi-fundamental/semi-empirical approach is consistent with recent trends in terms of the simulation or predictive modelling of metallurgical systems – which have been largely prompted by the increasing recognition of the limitations associated with pure empirical or thermodynamic approaches and methodologies.

Consistent with this hybrid type of approach, the identification and assessment of relevant and available empirical data and information pertaining to the system under investigation is considered an essential first-step in the proposed predictive methodology, and is strongly coupled to problem formulation. The starting point for this research project thus entailed the development of a solid mineral waste inventory database for the South African primary metal and coal-based power generation industry sectors.

Although currently incomplete and largely deficient in terms of available data, the inventory model structure developed in Section 2.1 of the report served to identify data and information requirements and provided an important starting point for the subsequent development of a methodological approach for addressing current data gaps and deficiencies. Together problem formulation (of which information collection is an integral part) and qualitative waste characterisation play a key role in determining what degree of effort is required (if any at all) in terms of quantitative waste characterisation and predictive modelling – both of which are significant and resource intensive undertakings. These preliminary steps in the methodology also provide decision-makers with key information, pertaining in particular to the likelihood and potential nature of adverse environmental effects, in the early stages of a project life cycle.

The outputs from waste characterisation and leachate generation modelling determine the time-dependant concentration profiles of mobile constituents at the interface between the waste deposit and the surrounding environment. Whilst it is necessary to also consider the fate of contaminants in the subsurface environment in order to predict impact, this will have little influence on the identification of impact minimisation opportunities. The treatment of subsurface hydrogeology and geochemical processes can thus be less rigorous and, unless the decision faced is one of site placement, the subsurface can be treated as a constant in the assessment. This is convenient, as generic data inputs to simple models (which are still representative of South African conditions) can be defaulted to. Furthermore, in contrast to models for leachate generation, fate and transport models have been the subjective of fairly extensive research and development over the past two decades. In line with this, Section 2.5 of the report developed a simple model case for situations where full physical and hydrogeological characterisation of the site is unavailable, using the well-established groundwater flow and mass transport codes MODFLOW and MT3D.

Finally, the proposed methodology condenses the spatially and temporally distributed contaminant concentration profiles, derived from leachate generation and dispersion modelling, into an appropriate decision-support indicator. The so-called “impacted land footprint (ILF)” indicator, developed in Section 2.6 of the report, gives an indication of the land area or volume impacted by the deposition of solid waste, and is derived by comparing the predicted environmental concentrations with levels believed to cause effects, such as water quality criteria. Section 2.6 also proposed approaches to reduce the number of footprints necessary to define the impact. These approaches include aggregation of the impacted land footprints by only including those for strategic constituents, (e.g. salinity and strategic metals) and methods to capture the time-dependant nature of the impacted land footprints (e.g. using snapshot, integral and characteristic parameter methods). Overall, this proposed ILF approach results in a midpoint indicator which is realistic, accurate and compatible with risk-based environmental assessment approaches. Further strengths of this approach are its practicality, transparency and relevance.

4.1.3 Observations from the case study

Chapter 3 of the report demonstrated the application of the generic predictive methodology and associated tools to the tailings output stream arising from the early beneficiation of porphyry-type copper sulphide ore deposits. The selection of this case study was based on the fact that it encompasses many of the complexities and problems typically associated with the mineral-based resource industries. These include complex chemical compositions; large volumes; and relatively high and protracted risks to the surrounding environment. In accordance with the generic methodology developed in Chapter 2 of the report, this case study was divided into a number of component main tasks and corresponding sub-tasks – the key outcomes of which are summarised here.

In line with the proposed impact prediction methodology, the collation of relevant and available data and information to describe the generic porphyry-type copper sulphide ore deposit → tailings deposit → leachate emissions system provided the starting point for this case study. The review and assessment conducted in Section 3.1 of the report confirmed the findings of previous investigators, i.e. that currently available data pertaining to primary metal production processes is incomplete, inconsistent and very uneven. The limitations and inconsistencies in currently available data and information, furthermore, pertain not only to the compositions of the waste output streams (waste rock and tailings), but also to the characteristics of the copper ore deposits from which they are generated, and the time-related emissions arising from their disposal. Nevertheless, the collation of available data played a key role in terms of informing subsequent case study tasks by providing a detailed qualitative understanding of the system under consideration (particularly with respect to the key factors and variables influencing the performance of such); serving to make existing data more accessible and comparable; and enabling current data gaps and deficiencies to be clearly identified.

Qualitative characterisation of generic porphyry-type copper sulphide tailings was subsequently carried out in Section 3.2 to address the above-mentioned data gaps and deficiencies, and provide information which guides and supports subsequent empirical waste characterisation and predictive modelling studies. This entailed firstly predicting the chemical characteristics of generic porphyry-type copper sulphide tailings on the basis of their origins (i.e. characteristics of typical porphyry-type copper sulphide ores), and an understanding of the distribution behaviour of ore components during milling and flotation (i.e. the source of the waste). Key characteristics of potential environmental significance in the case of generic porphyry-type copper sulphide tailings were subsequently identified on the basis of the hazardous properties and relative mobilities of the constituents in a typical disposal scenario. Whilst the predicted inventory lists, generated within Section 3.2 of the report, are considerably more complete and less dispersed than those compiled on the basis of available historical data alone, levels of uncertainty remain relatively high – especially that pertaining to generic data on porphyry-type copper sulphide ore deposits, and consequently the output streams arising from subsequent milling, flotation and tailings deposition. This can be attributed largely to the variation in the concentrations of elements between ore deposits, and even between different zones within the same deposit, as a function of local geology, hydrology and climatology. Nevertheless, the generic qualitative characterisation case study conducted here provided data and information of key significance in terms of early stage decision-making, as well as further data collection and impact prediction studies. In particular, the generic qualitative predictions indicated that a number of the chalcophilic co-elements (i.e. elements commonly occurring as sulphide minerals in non-oxidising environment), as well as the siderophilic co-elements (i.e. elements generally occurring as either sulphides or uncombined form - PGMs, Au and Ag) occurring within copper sulphide ore deposits may be enriched to a significant extent relative to their average crustal abundance, some to an even greater extent than the targeted copper metal. Many of the chalcophilic metals and semi-metals are toxic at “high” to “severe” levels and, although their subsequent deportment to the tailings waste stream during early beneficiation is only partial (< 30%), they can still occur in environmentally significant concentration levels. This is particularly the case for As, Zn, Cd, Se, Cu and Sb. Other constituents of potential environmental significance include Fe, Ni, Si and, in particular, manganese and sulphate. Apart from the environmental significance of strategic constituents on an individual basis, the generic qualitative characterisation study also emphasised the need to consider other environmental categories of potential concern in terms of waste outputs from the early beneficiation of base metal sulphide ore deposits, namely salinity and acidity.

The next task in the case study after generic qualitative waste characterisation involved empirical characterisation of a specific flotation tailings sample, freshly prepared on a laboratory-scale from a typical porphyry-type copper sulphide run-of-mine ore. The objectives of this specific project task were three-fold, namely: 1) to guide and inform subsequent predictive modelling studies; 2) to assess the validity and/or limitations of the generic qualitative predictions; and 3) to identify opportunities to optimise current methodologies and protocols for the effective and reliable empirical characterisation of porphyry-type copper, and other base metal sulphide wastestreams. These objectives were achieved through the application of a number of analytical and “static” laboratory waste characterisation methodologies, conducted in the form of a systematic protocol which allowed for validation of the consistency of results between the various methodologies. Specific techniques applied in this case study task included techniques for the quantification of the relevant physical properties; analytical techniques for quantification of total element concentrations; analytical techniques for the quantification of mineralogical compositions; sequential chemical extraction (SCE) tests to determine the partitioning or distribution of elements; and tests designed to determine the capacity of a waste to generate or neutralise acid.

Apart from generating quantitative predictive model input data (e.g. concentrations of elements and mineral phases, and actual physical properties), the empirical characterisation programme outlined in Section 3.3 (in combination with the outcomes of the previous case study tasks) also provided valuable information with respect to the strategic components of potential environmental significance, as well as the key reaction mechanisms and parameters controlling their release in a disposal environment. This information is summarised within Figure 4.1

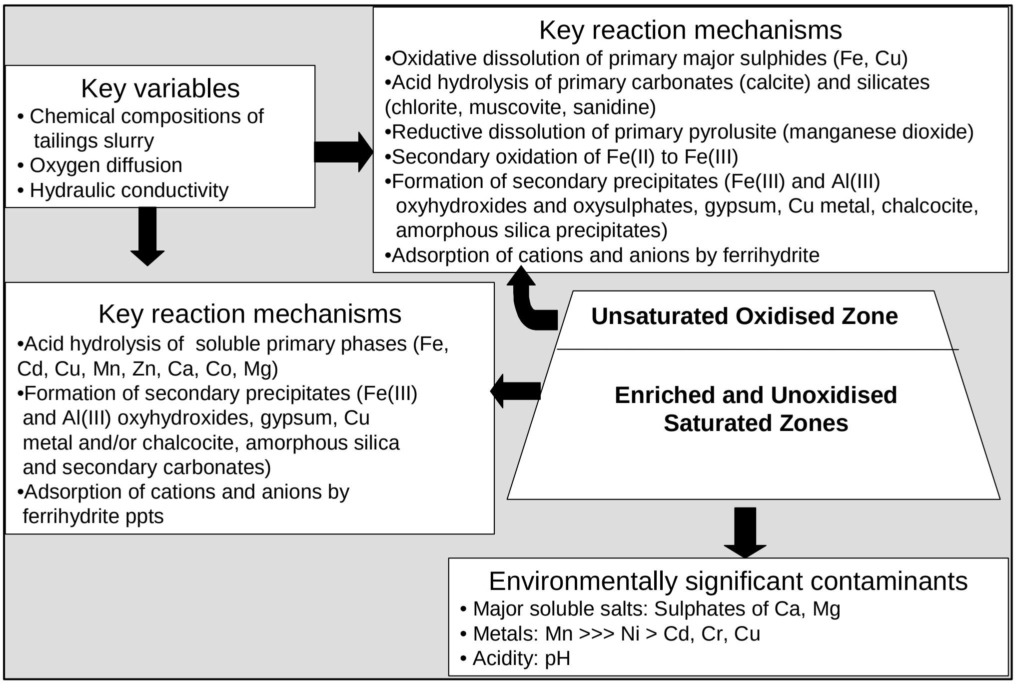


Figure 4.1: Key characteristics of a porphyry-type copper sulphide tailings impoundment

Although the testwork indicated that this copper sulphide tailings sample has a relatively high acid generating capacity, kinetic Net Acid Generating (NAG) tests indicated that the overall acid generating mechanisms are slow. The pH of the pore waters in the oxidation zone of the tailings impoundment will thus probably decrease gradually as the rate and extent of sulphide oxidation increases and the relatively soluble acid neutralising carbonate compounds become depleted.

The empirical testwork programme also demonstrated that, although there is still considerable uncertainty associated with current Sequential Chemical Extraction (SCE) test protocols in terms of selectivity, this technique provides valuable information pertaining to the forms, and approximate concentrations, of trace-minor element phases (which are difficult to detect and quantify using conventional mineralogical techniques). It is also a useful tool in the identification of strategic elements of potential environmental significance. In terms of current laboratory-scale tests for the determination of acid generating capacity, investigations by Maluleke (2006) have indicated that neither the original Sobek (1978) Acid Base Accounting (ABA) method, nor the single stage Net Acid Generation (NAG) method, provide a sufficiently accurate and reliable measure of the potential acid generating capacity in the case of porphyry-type copper sulphide tailings. Sequential and kinetic NAG tests are thus recommended to determine the time-related acid generating potential of this type of waste material. A simple modified ABA test, involving a single addition of H_2O_2 during determination of the acid neutralising capacity, can, however, be applied as a preliminary screening exercise. This case study also demonstrated the contribution of the qualitative generic predictions, with respect to both the design of the empirical waste characterisation programme and interpretation of the derived results. In general the generic qualitative information predicted on the basis of the basis of the tailings origins and source, were in fairly good agreement with the results of the empirical waste-specific characterisation tests. Discrepancies, particularly in terms of the concentrations of Al, Na, Se and B in the tailings, could be attributed largely to variations in the characteristics of generic ore deposits.

Finally, the derived waste characterisation and management data was used to quantify the water-related impacts associated with this copper tailings sample – by means of quantitative predictive modelling of the time-related generation and dispersion of contaminated leachate, and the subsequent derivation of an associated impacted land footprint indicator for decision-support purposes. In order to achieve this objective, the generic leachate generation model structure first needed to be expanded in terms of incorporating the relevant reaction mechanisms and parameters of particular relevance to this waste type. Particular emphasis was placed on modelling pyrite oxidation, and in addressing shortcomings associated with standard “shrinking core” kinetics.. Together with the hydrodynamic representation of the generic waste deposit, the modified shrinking core model developed in Section 3.4 of the report provided a more sophisticated and accurate description of pyrite oxidation in waste deposits. A simple case study was subsequently conducted to compare saturated and unsaturated tailings deposits, and to investigate the effects of reduced hydraulic conductivity and oxygen diffusion through the application of an impoundment cover. The role of the impact prediction modelling in this case was thus not to quantify absolute impact, but rather to give an indication of relative impact arising from tailings management between the possible scenarios in order to demonstrate the impact assessment methodology. The leachate generation model presented here successfully captures the significant leach behaviour of porphyry-type copper sulphide tailings. The kinetic processes included in the model are sulphide oxidation, abiotic and biotic ferrous ion oxidation and; calcite and silicate mineral dissolution. Important equilibrium processes including secondary mineral precipitation are incorporated by interfacing with a proven solution speciation program (MINTEQA2) while detailed waste characterisation provided the necessary input parameters for the model. As this case study represents a hypothetical situation, generic data inputs for sandy aquifer types have been defaulted to in the case of fate and transport modelling. The unsaturated and uncovered deposit was found to result in the largest metals (as represented by iron) and salinity impacted land footprints, as a direct result of the higher leachate concentrations and larger deposit area. There was no discernable salinity or iron footprint for this particular tailings sample (i.e. with a sulphide sulphur and pyrite content of < 5 %) in a saturated and covered disposal scenario.

4.2 Recommendations for Further Work

Whilst the potential overall value of the approach for the quantitative prediction of solid mineral waste impacts has been clearly demonstrated, further expansion and optimisation will increase both the confidence in, and usefulness of, the methodologies and criteria developed within this project. This section aims to identify these requirements and direct future research efforts, so as to increase the robustness, acceptance and, ultimately, the practical application of the proposed approach.

4.2.1 Optimisation of current solid impact assessment support-tools

Specific recommendations in terms of improving the information collection, management and generation of data and information which underpins the proposed predictive approach, include:

- *Expansion and upgrading of the mineral waste inventory database*

  The current mineral waste inventory database has been compiled on the basis of readily available data and information, and it is recognised that there is still scope to add to this database significantly through existing information sources. Such sources include waste characterisation testing; direct communication with waste generators and other research organisations; general literature; and specialised reports.

- *Improved characterisation and classification of ore deposits*

  This study has identified that the poor quality of available data pertaining to the parent ore (both in terms of accuracy and detail) is one of the major limiting factors of the qualitative waste characterisation step. The availability of more detailed and reliable empirical data pertaining to the chemical compositions of typical run-of-mine ores from the various industry sectors, as well as a better understanding of the relationship between the characteristics of ores and their genesis, will greatly enhance the quality of feed-forward predictions in accordance with the predictive methodology developed here. Confidence in terms of the quality of feed-forward predictions of element distribution factors during ore processing will be further enhanced through the application of validation exercises, in which predicted data ranges are compared with empirically-derived compositions of inputs and outputs across unit reactors.

- *Optimisation of current sequential chemical extraction (SCE) test methods*

  Testwork carried out under this project has confirmed that, although this technique has the potential to complement conventional mineralogical techniques (such as XRD) in terms of both identifying and quantifying trace-minor element phases, further developmental work on the selectivity of the various extraction steps is still required.

4.2.2 Future application of the proposed approach – the way forward

There are several opportunities to take this work further, both in terms of the scope of work addressed, and in terms of practical tools which could be developed in order to facilitate the uptake of the approach. There is particular merit in considering the following additional tasks:

- Improving the quality and comprehensiveness of the database which links ore composition and mineralogy to waste profiles and environmental impacts. This is best achieved through active partnerships with industry, as the generic data available in the public domain is of doubtful real value.
- Performing additional case studies on targeted metals. The copper case study undertaken in this project, whilst indicative of the potential of this approach, needs to be augmented by other case studies which are relevant to the regional context. For example, the focus on acid bearing wastes could be extended to look at overburden from iron-ore processing, coal stockpiles, tailings etc. Other critical wastes, such as gold tailings, are of interest too. However, a case study in this area would require additional modelling work to incorporate specific reactions such as cyanidation.
- Taking the analysis to a site-specific level. Here one would need to consider local information pertaining to site hydro-geology, catchment geography; local climatology; ore composition etc. In so doing, it will be possible to link this approach to other environmental planning and assessment tools, such as Environmental Impact Assessment.

- Giving consideration to the use to which the assessment of environmental impact will be put. For example, if the focus is on water quality, then there is value in isolating impacts to surface and ground water. If the focus of the assessment is more generally on land use, then there is a need to understand how pollution plumes can be integrated with more traditional measures of land-related impacts, such as biodiversity and soil quality.
- Generating a better understanding of the time dimension of this analysis. For example, the whole notion of possible discounting of effects over time needs to be considered. Also, whether there should be a focus on chronic versus acute impacts, or some balance of these.

Application of the developed approach and associated methodologies is not a trivial undertaking and requires fairly extensive technical expertise and knowledge. Technology transfer to third parties will require continued input from dedicated specialists. In order to maximise the usefulness and acceptance of this approach within the mineral resource-based industry sectors, it is recommended that the knowledge gained through this study be captured in the form of a set of practical decision support tools, which:

(i) Generate and collate data and information pertaining to the compositions of input/output streams; key factors of environmental and economic significance; and potential environmental impact as a function of ore composition, process technologies and/or waste management practices.

(ii) Guide the selection, design and application of empirical methodologies and predictive models in accordance with industry sector, associated waste “types” and the decision context.

(iii) Link the impacted land footprint indicator to other decision-support tools and protocols (e.g. Life Cycle Assessment, Design for the Environment, Environmental Risk Assessment) and information management tools (e.g. GIS)

(iv) And seek to see these tools applied to a wide range of decision contexts such as mine planning, operation and closure; catchment management; and land use planning.

With its focus on all critical aspects of decision making, this set of tools can be thought of as a dynamic expert system which would find value amongst policy makers, mine planners, and minerals processing companies.

4.3 Closing Statement of Significance

Limitations and developmental requirements aside, the methodology developed in this study addresses many of the deficiencies associated with current approaches, thus enabling more accurate and reliable assessments of the potential environmental impacts from the primary industries. In particular, the stepwise methodology recognises and assimilates the time-dependant and spatially-distributed nature of the solid waste impacts, and makes significant advance in terms of modelling the complex physical transport processes (including fluid flow and gas diffusion mechanisms) typical of full-scale solid mineral waste deposits. Model outputs are interpreted in the form of an easily measured proxy or mid-point indicator – the impacted land footprint indicator – which avoids the complexities, controversies and uncertainties typically associated with detailed exposure modelling whilst still attaining an indication of risk. In addition, the supporting waste characterisation and predictive modelling protocols are relatively simple yet scientifically rigorous – being underpinned by a comprehensive understanding of the key mechanisms and influencing parameters governing the behaviour and distribution of elements across the ore formation → ore extraction & beneficiation → solid waste disposal → leachate generation → leachate dispersion → environmental impact mechanistic chain.

In terms of its potential value to the primary industries, the proposed approach facilitates identification of opportunities for process improvements that minimise both the quantities and hazardous nature of the waste – in line with the synonymous principles of cleaner production and sustainable development. This can be attributed to the fact that the conceptual methodology focuses on the fundamental steps in the causal mechanistic chain, thus enabling potential environmental impacts to be linked back to the waste management strategies and generating processes themselves. What follows is the ability to influence and control behaviour, and eventually optimise waste management and the environmental performance of the process as a whole. The proposed approach is also of potential application in environmental policy-making, particularly in terms of the establishment of industrial buffer zones, and appropriate land-use applications

Another valuable feature and key strength of the approach is its ability to adapt to the different decision contexts and levels of data availability throughout a project life cycle (see Figure 4.2).

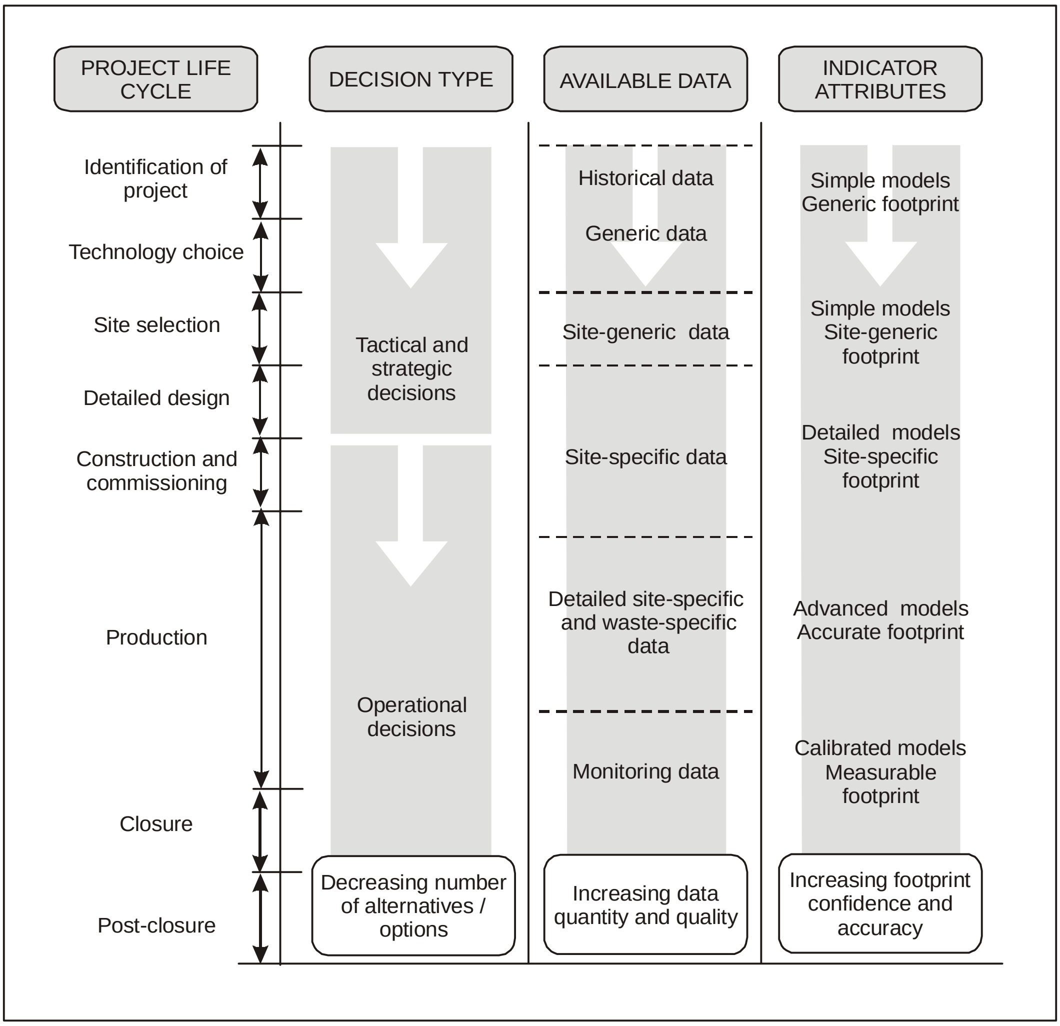


Figure 4.2: Decision types for the primary industries – data availability and impacted land footprint indicator confidence and accuracy mapped onto the project life cycle

In preliminary project phases involving tactical and strategic decisions, the footprint indicator is based on simple models that use generic and qualitative data. A footprint indicator based on these generic inputs can be used to distinguish between different technology options, different sites (based on site-generic data) and different waste management strategies. During production stages, the impacted land footprint can be calculated using increasingly site-specific data and models to improve waste management and evaluate rehabilitation, treatment and control strategies to minimise long-term liability. Monitoring data can eventually be used to calibrate models, further increasing the confidence in (and accuracy of) the footprint indicator and associated models. This hierarchical approach to impact predictions ensures that information and data requirements remain manageable, and the necessary data integrated into the early decision stages of a project life cycle in a manner that is both time and cost effective.

REFERENCES

Abollino, O; Aceto, M; Malandrino, M; Mentasti, E; Sarzanini, C and Barberis, R (2001) Distribution and mobility of metals in contaminated sites. Chemometric investigation of pollutant profiles. *Environmental Pollution*, In press.

ACMER (Australian Centre for Minerals Extension and Research) (2006) *An Integrated Systematic Approach to Sustainable Mine Closure.* Workshop held at Pokolbin, New South Wales.

Al, TA and Blowes, DW (1999) The hydrogeology of a tailings impoundment formed by central discharge of thickened tailings: Implications for tailings management. *Journal of Contaminant Hydrology*, **38**, 89-505.

Al, TA; Martin, CJ and Blowes, DW (2000) Carbonate-mineral- water interactions in sulphide-rich mine tailings. *Geochimica et Cosmochimica Acta*, **6**(23), 393-39.

Al-Dahhan, MH and Dudukovic, MP (1995) Catalyst wetting efficiency in trickle-bed reactors at high pressure. *Chemical Engineering Science,* **50**, 2377-2389.

Allison, JD; Brown, DS and Novo-Gradac, KJ (1990) MINTEQA2/PRODEFA2-A geochemical assessment model for environmental systems. *User's Manual*, Version 3.0.

AMIRA (2002) *ARD Test Handbook: Prediction and Kinetic Control of Acid Mine Drainage.* AMIRA International, (Melbourne, Australia) (available at www.amira.com.au).

Anderson, MP and Woessner, WW (1992) *Applied groundwater modelling - simulation of flow and advective transport.* Academic Press Inc., USA.

Anderson, MP; Ward, DS; Lappala, EG and Prickett, TA (1993) Computer models for subsurface water. In DR Maidment (Ed.), *Handbook of Hydrology*, Chapter 22. McGraw-Hill, New York.

Ansto (Australian Nuclear Science and Technology Organisation) (1995) Managing mine wastes: Quantifying acid rock drainage and ecological risk. *A short course*.

ANZECC (Australia and New Zealand Environment and Conservation Council) (1999) *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*: Draft.

Aso, M; Iyama, Y and Yabe, T (1984) Saganoski smelter and refinery today. *Metallurgical Review of MMIJ*, **1**, 134-149.

Atkinson, SF; Canter, LW and Ravan, MD (2006) The influence of incomplete or unavailable information on environmental impact assessment in the USA. *Environmental Impact Assessment Review*, **26**, 448-467.

Audigane, P; Gaus, I; Pruess, K and Xu, T (2006) *Modelling study of CO_2 storage at Sleipner (North Sea) using TOUGHREACT.* In: Proceedings, TOUGH Symposium 2006. Lawrence Berkeley National Laboratory, Berkeley, California.

Ayres, R; Ayres, L and Rǻde, I (2002) *The Life Cycle of Copper, it's Co-products and By-products*. MMSD.

Bain, JG; Blowes, DW; Robertson, WD and Frind, EO (2000) Modelling of sulphide oxidation with reactive transport at a mine drainage site. *Journal of Contaminant Hydrology,* **41**, 23-47.

Ball, JW and Nordstrom, DK (1991) WATEQ4F- User's manual with revised thermodynamic database and test cases for calculating speciation of major, trace and redox elements in natural waters. *US Geological Survey Open-File Report, 90-129*.

Banwart, SA and Malmstrő̋m, ME (2001) Hydrochemical modelling for preliminary assessment of minewater pollution. *Journal of Geochemical Exploration*, **74**, 73-97.

Barbour, AK and Shaw, IC (2000) Ecotoxicological impacts of the extractive industries. In A Warhurst and L Noronha (Ed.), *Environmental Policy in Mining: Corporate Strategy and Planning for Closure* (pp. 58-80). CRC Press.

Basson, L and Petrie, J (2001) A roadmap for decision making in different design contexts. *6th World Congress of Chemical Engineering,* Melbourne.

Battey, MH (1981) *Mineralogy for Students*. Longman.

Bendell-Young, LI; Thomas, CA and Stecko, JRP (2001) Contrasting the geochemistry of oxic sediments across ecosystems: a synthesis. *Applied Geochemistry*, In press.

Benner, SG; Gould, WD and Blowes, DW (2000) Microbial populations associated with the generation and treatment of acid mine drainage. *Chemical Geology*, **169**, 435-48

Benzaazoua, M; Marion, P; Liouville-Bourgeois, L; Joussemet, R; Houot, R; Franco, A and Pinto, A (2002) Mineralogical distribution of some minor and trace elements during a laboratory flotation processing of Neves-Corvo ore (Portugal). *International Journal of Mineral Processing*, **66**, 163-181.

Bermond, A (2001) Limits of sequential extraction procedures re-examined with emphasis on the role of H+ ion reactivity. *Analytica Chimica Acta*, **445**, 79-88.

Bezuidenhout, N and Rousseau, PDS (2005) An investigation into the depth and rate of weathering on gold tailings dam surfaces as key information for long-term AMD risk assessments. *WRC Report Number 1347/1/05.* WRC, South Africa.

Biswas, A and Davenport, W (1994) *Extractive Metallurgy of Copper*. Pergamon.

Blowes, DW; Jambor, JL and Hanton-Fong, CJ (1998) Geochemical, mineralogical and microbiological characterization of a sulphide-bearing carbonate-rich gold-mine impoundment, Joutel, Quebec. *Applied Geochemistry,* **13**(6), 687-705.

Blowes, DW; Ptacek, CJ and Jurjovec, J (2003) Mill tailings: Hydrogeology and geochemistry. In. JL Jambor, DW Blowes and AIM Ritchie (Ed.), *Environmental Aspects of Mine Wastes: Short Course Series 31.* Mineralogical Society of Canada, 95-116.

Boer, RH and Pinetown, KL (2006) A quantitative evaluation of the model distribution of minerals in coal deposits in the Highveld area and the associated impact on the generation of acid and neutral mine drainage. *WRC Report Number 1264/1/06*. WRC, South Africa.

Boulding, JR (1995) *Practical handbook of soil, vadose zone and ground water contamination: assessment, prevention and remediation.* Lewis Publishers, Boca Raton.

Bourg, ACM (1995) Speciation of heavy metals in soils and groundwater and implications for their natural and provoked mobility. In W Salomons, U Forstner and P Mader (Ed.), *Heavy Metals-Problems and Solutions.* Springer-Verlag.

Bridge, G (2000) The Decommissioning of leach dumps and protection of water quality: Lessons for best practice from copper and gold leaching operations in the United States. In A Warhurst and L Noronha (Ed.), *Environmental Policy in Mining: Corporate Strategy and Planning for Closure* (pp. 33-55). CRC Press.

Brookfield, AE; Blowes, DW and Mayer, KU (2006) Integration of field measurements and reactive transport modelling to evaluate contaminant transport at a sulphide mine tailings impoundment. *Journal of Contaminant Hydrology*, in press.

Brookins, DG (1988) *Eh-pH Diagrams for Geochemistry*. Springer-Verlag.

Brzezicka, M and Baranowska, I (2001) Methods for separation of trace amounts of platinum and investigation of the influence of interfering elements during platinum determination in copper ores and copper concentrates by graphite furnace atomic adsorption spectrometry. *Spectrochimica Acta Part B*, **56**, 2513-2520.

Broadhurst, JL (2006) Generalised strategy for predicting environmental characteristics of solid mineral waste – A focus on copper. *PhD thesis dissertation, University of Cape Town, South Africa (in press.*

Broadhurst, JL; Petrie, JG and von Blottnitz, H (2006) Understanding element distribution during primary metal production. *Green Processing Conference*, Newcastle, Australia.

Brown, PL; Ritchie, IM; Bennett, JW; Comarmond, MJ and Timms, GP (2000) Geochemical kinetic modelling of acid rock drainage. In *ICARD 2000 - International Conference on Acid Rock Drainage.* Denver, USA.

Bruckard, W and Woodcock, J (2004) Characterisation of metal-containing waste products in relation to pretreatment methods for metal recovery and recycling. *Green Processing 2004* (pp. 217-224).The Australasian Institute of Mining and Metallurgy, Fremantle.

Buchter, AR; Cropp, A; French, D and Gottlieb, P (2004) Introducing a new coal analysis capability, *10th South African Conference on Coal Science and Technology Indaba*, Johannesburg.

Bulatovic, S (1997) Flotation behaviour of gold during processing of porphyry copper-gold ores and refractory gold-bearing sulphides. *Minerals Engineering*, **10**, 895-908.

Bulatovic, SM; Wyslouzil, DM and Kant, C (1998) Operating practices in the beneficiation of major porphyry copper/molybdenum plants from Chile: Innovated technology and opportunities, a review. *Minerals Engineering*, 11(4), 313-331.

Cano-Ruiz, JA and McRae, GJ (1998) Environmentally conscious chemical process design. *Annu. Rev. Energy Environ*., **23**, 499-536.

Canterford, JH (1985) Hydrometallurgy: Winning metals with water. *Chemical Engineering*, 41-49.

Cardoso, FE and Martin, H (1986) The selective extraction of Pb and Zn in selected mineral and soil samples, application in geochemical exploration (Portugal), *J. Geochem. Exploration*, **26**, 231-248.

Carlsson, E; Thunberg, J; Őhlander, B and Holmstrőm, H (2002) Sequential extraction of sulphide-rich tailings remediated by the application of till cover, Kristineberg mine, northern Sweden. *The Science of the Total Environment*, **299**, 207-226.

Chao, TT and Zhou, L (1983) Extraction techniques for selective dissolution of amorphous iron oxides from soils and sediments. *Journal of Soil Science Soc. Am. Proc*, **47**, 225– 232.

Cheng, H-P and Yeh, G-T (1998) Development and demonstrative application of a 3-D numerical model of subsurface flow, heat transfer, and reactive chemical transport: 3DHYDROGEOCHEM. *Journal of Contaminant Hydrology,* **34**, 47-83.

Chiang, W-H and Kinzelbach, W (2001) *3D-Groundwater Modeling with PMWIN*. Springer-Verlag, Berlin.

Christie, A (2002) Water management in coal mining: Legacies, practises and strategies. *Mine Water Management*, 30-32.

Coetzee, H; Winde, F and Wade, PW (2006) An assessment of sources, pathways, mechanisms and risks of current and potential future pollution of water and sediments in gold-mining areas of the Wonderfonteinspruit catchment. *WRC Report Number 1214/1/06.* WRC, South Africa.

Coetzer, G; du Preez, HS and Bredenham, R (2003) Influence of water resources and metal ions on galena flotation of Rosh Pinah ore. *The Journal of the South African Institute of Mining and Metallurgy,* **103**(3), 193-207.

Cohen, B; Lewis, AE; Petersen, J; von Blottnitz, H; Drews, SC and Mahote, SI (1999) The TCLP and its applicability for the characterisation of worst case leaching of wastes from mining and metallurgical operations. *Advances in Environmental Research*, **3**(2), 152-165.

Correns, CW (1969) *Introduction to Mineralogy: Crystallography and Petrology*. George Allen & Unwin Ltd.

Cotton, FA and Wilkinson, G (1962) *Advanced Inorganic Chemistry: A Comprehensive Text*. Interscience Publishers.

Cox, DP; Lindsey, DA; Singer, DA; and Diggles, MF (2003) *Sediment-Hosted Copper Deposits of the World: Deposit Models and Databases.* US Geological Survey

Cox, DP and Singer, DA (2003) *Mineral Deposit Models.* US Department of the Interior and US Geological Survey

Crock, JG; Arbogast, BF and Lamothe PJ (1999) Laboratory methods for the analysis of environmental samples. In *The Environmental Geochemistry of Mineral Deposits, Part A: Processes, Techniques and Health Issues*, Vol. 6A, Chapter 13. (pp 265-287). Society of Economic Geologists, Chelsea, MI.

Cussler, EL (1997) *Diffusion - mass transfer in fluid systems.* Cambridge University Press, Cambridge, United Kingdom.

Dallas, HF and Day, JA (1993) The effect of water quality variables on riverine ecosystems: A review. *Water Research Commission Report*, **TT61/93**, Water Research Commission, Pretoria.

Dang, Z; Liu, C and Haigh, MJ (2002) Mobility of heavy metals associated with the natural weathering of coal mine spoils. *Environmental Pollution*, **118**(3), 419-426.

Danielson, L and Nixon, M (2000) Current regulatory approaches to mine closure in the United States. In A Warhurst and L Noronha (Ed.), *Environmental Policy in Mining: Corporate Strategy and Planning for Closure* (pp 311-350). CRC Press.

Davis, GB and Ritchie, AIM (1986) A model of oxidation in pyritic mine wastes: Part 1: Equations and approximate solution. *Applied Mathematical Modelling,* **10**, 314-322.

Dhar, BB (2000) Environmental management systems for closure and best practice in the Indian mining industry. In A Warhurst and L Noronha (Ed.), *Environmental Policy in Mining: Corporate Strategy and Planning for Closure* (pp. 295-310). CRC Press.

Dixon, DG (2003) Heap leach modeling – the current state of the art. In: *Proceedings of the 2003 International Symposium on Hydrometallurgy in Honour of Ian Ritchie.* Vancouver, B.C. Canada.

DME (South African Department of Minerals & Energy) (2003) Annual Report, Department of Minerals and Energy, South Africa.

Dold, B and Fontbote, L (2001) Element cycling and secondary mineralogy in porphyry copper tailings as a function of climate, primary mineralogy, and mineral processing. *Journal of Geochemical Exploration*, **74**, 3-55.

Dold, B (2003) Speciation of the most soluble phases in a sequential extraction procedure adapted for geochemical studies of copper sulfide mine waste. *Journal of Geochemical Exploration*, **80**, 55–68.

Domenico, PA and Schwartz, FW (1997) *Physical and chemical hydrogeology.* John Wiley & Sons, New York.

Dreisinger, D (2003) Total pressure oxidation of copper concentrates: Heat and material balance. *MSc Hydrometallurgy Course Lecture Notes,* University of Cape Town.

Du Bray, EA (1996) *Preliminary Compilation of Descriptive Geoenvironmental Mineral Deposit Models.* US Geological Survey.

Ďuďa, R and Rejl, L (1986) *Minerals of the World*. Arch Cape Press, New York.

DWAF (South African Department of Water Affairs and Forestry) (1996) *South African Water Quality Guidelines.*

DWAF (South African Department of Water Affairs and Forestry) (1998) *South African National Water Act* (No 38).

DWAF (South African Department of Water Affairs and Forestry) (2002) *Environmental Management Framework*, First Draft.

Eary, LE; Rai, D; Mattigod, SV and Ainsworth, C (1990) Geochemical factors controlling the mobilisation of inorganic constituents from fossil fuel combustion residues II: Review of minor elements. *Journal of Environmental Quality*, **19**, 202-214.

EEA (European Environmental Agency) (1997) Life cycle assessment: a guide to approaches, experiences and information sources. *Environmental Issues Series No 6.*

EEA (European Environmental Agency) (1998) Computer based models in integrated environmental assessment. *Technical Report No 1.*

Environment Australia (1997) *Best Practice Environmental Management in Mining. Managing Sulphide Mine Wastes and Acid Drainage.*

Environment Canada Waste Water Technology Centre (1990) *Compendium of Waste Leaching Tests.*

Fällman, A and Aurell, B (1996) Leaching tests for environmental assessment of inorganic substances in wastes, Sweden. *The Science of the Total Environment*, **178**, 71-84.

Fanfani, L; Zuddas, P and Chessa, A (1997) Heavy metals speciation analysis as a tool for studying mine tailings weathering. *Journal of Geochemical Exploration*, **58**, 241-248.

Finkelman, RB; Giffin, DE (1986) Hydrogen peroxide oxidation: an improvement of methods for rapidly assessing acid-generating potential of sediments and sedimentary rocks, *Recreation and Revegetation Research*, **5**, 521 – 534.

Flett, D; Gibbon, A and Pexton, H (1996) Treatment options for waste from metallurgical operations: A technical review, *Technical Review Series,* No 19, Mineral Industry Research Organisation, London.

Fogler, HS (1992) *Elements of chemical reaction engineering.* Prentice-Hall Inc., New Jersey.

Fonseca, EC and da Silva, EF (1998) Application of selective extraction techniques in metal-bearing phases identification: a South European case study. *Journal of Geochemical Exploration*, **61**, 203–212

Freeze, RA and Cherry, JA (1979) *Groundwater.* Prentice-Hall, New Jersey.

Froment, GF and Bischoff, KB (1979) *Chemical reactor analysis and design,* John Wiley & Sons, New York.

Gaines, L. (1980) *Energy and Material Flows in the Copper Industry*. US Department of Energy.

Galan, E; Gomez-Ariza, JL; Gonzalez, I; Fernandez-Caliani, JC; Morales, E and Giraldez, I (2002) Heavy metal partitioning in river sediments severely polluted by acid mine drainage in the Iberian Pyrite Belt. *Applied Geochemistry*, in press,

Garrabrants, AC and Kossson, DS (2000) Use of a chelating agent to determine the metal availability for leaching from soils and wastes. *Waste Management*, **20**, 155-165.

Garrels, RM (1960) *Mineral Equilibria at Low Temperature and Pressure*. Harper & Brothers Publishers, New York

Gatehouse, S; Roussel, DW and van Moort, JC (1977) Sequential soil analysis in exploration analysis. *Journal of Geochemical Exploration*, **8**, 483–494.

Gaus, I; Azaroual, M and Czemichowski-Lauriol, I (2006) *Reactive Transport modelling of dissolved CO2 in the cap rock base during CO2 sequestration (Sleipner Site, North Sea)*. Report, BRGM (French Geological Survey), France

Gerke, HH; Molson, JW and Frind, EO (1998) Modelling the effect of chemical heterogeneity on acidification and solute leaching in overburden mine spoils. *Journal of Hydrology,* **209** (1-4), 166-185.

Grove, DB and Stollenwerk, KG (1987) Chemical reactions simulated by groundwater quality models. *Water Resources Bulletin,* **23** (4), 601-615.

Grundy, C (1997) Obeying the ground rules. *Chemistry in Britain.*

Giurco, DP; Stewart, M and Petrie, JG (2000) The role of LCA in performance assessment in minerals processing-A copper case study. *SWEMP 2000*, Calgary, Canada.

Gunsinger, MR; Ptacek, CJ; Blowes, DW and Jambor, JJ (2006) Evaluation of long-term sulphide oxidation processes within pyrrhotite-rich tailings, Lynn Lake, Manitoba. *Journal of Contaminant Hydrology*, **83**, 149-170.

Habashi, F (1982) Hydrometallurgy. *Chemical & Engineering News*, **60**, 46-58.

Hage, JLT and Mulder, E (2004) Preliminary assessment of three new European leaching tests. *Waste Management*, **24**, 165-172.

Hall, GEM; Vaive, JE; Beer, R and Hoashi, M (1996) Selective leaches revisited, with emphasis on the amorphous Fe oxyhydroxide phase extraction. *Journal of Geochemical Exploration*, **56**, 59–78.

Han, FX; Banin, A and Triplett, GB (2001) Redistribution of heavy metals in arid-zone soils under a wetting-drying cycle soil moisture regime. *Soil Science*, 18–28.

Hansen, Y; Notten, PJ and Petrie, JG (2002a) A life cycle impact assessment indicator for ash management in coal-based power generation. *Journal of the South African Institute of Mining and Metallurgy,* **102** (5), 299-306.

Hansen, Y; Notten, PJ and Petrie, JG (2002b) The environmental impact of ash management in coal-based power generation. *Applied Geochemistry,* **17**, 1131-1141.

Hansen, Y (2004) Environmental impact assessment of solid waste management in the primary industries- A new approach. *PhD thesis dissertation, University of Sydney, Australia.*

Hansen, HK; Yianatos, JB and Ottosen, LM (2005) Speciation and leachability of copper in mine tailings from porphyry copper mining: Influence of particle size. *Chemosphere,* **60**, 1497-1503.

Hayes, P (1985) *Process Selection in Extractive Metallurgy*. Hayes publishing Co, Brisbane

Heijungs, R (1995) Harmonisation of methods for impact assessment. *Envir. Sci. & Pollut Res*. **2** (4), 217-224.

Hertwich, EG; Pease, WS and McKone, TE (1998) Evaluating toxic impact assessment methods: what works best? *Environmental Science & Technology*, **32**(5): A128-A144.

Hutson, JL and Wagenet, RJ (1995) The application of chemical equilibrium in solute transport models. *Soil Sciences of America,* Special Publication No 42.

ICMM (1995) *Risk Assessment and Risk Management of Non-Ferrous Metals: Realising the Benefits and Controlling the Risks*.

ICMM (2002) The mining and metals industries: Progress in contributing to sustainable development. *A Working Paper.*

Iliuta, I; Larachi, F and Grandjean, BPA (1999) Residence time, mass transfer and back-mixing of the liquid in trickle flow reactors containing porous particles. *Chemical Engineering Science,* **54**, 4099-4109.

Jaebong J (2003) Solid-phase speciation of copper in mine wastes. *Bull. Korean Chem. Soc*., **24**(2), 209-218.

Jarvis, AP and Younger, PL (2000) Broadening the scope of mine water environmental impact assessment: A UK perspective. *Environmental Impact Assessment Review*, **2**, 2000, 85-96.

Jones, DR (1995) The leaching of major and trace elements from coal. In DJ Swaine and F Goodarzi (Ed.), *Environmental Aspects of Trace Elements in Coal* (pp. 221-262). Kluwer Academic Publishers, Netherlands.

Jurjovec, J; Ptacek, CJ and Blowes, DW (2002) Neutralisation mechanisms and metal release in mine tailings: A laboratory column experiment. *Geochemical et Cosmochimica Acta*, **66**(9), 1511-1523.

Kelly, EG and Spottiswood, DJ (1982) *Introduction to Mineral Processing*. John Wiley & Sons.

King, J; Dreisinger, D; and Knight, D (1993) The total pressure oxidation of copper concentrates. In R Reddy and R Wiezenbach (Ed.), *Extractive Metallurgy of Copper, Nickel and Cobalt* (pp 735-756). The Minerals, Metals and Materials Society.

Kirby, CS; Thomas, HM; Southam, G and Donald, R (1999) Relative contributions of abiotic and biological factors in Fe(II) oxidation in mine drainage. *Applied geochemistry*, **14**, 511-530.

Kirkpatrick, C and Lee, N (1999) Integrated appraisal and decision making. Environmental Impact Assessment Review, **19**, 27-232.

Knox, RC, Sabatini, DA and Canter, LW (1993) *Subsurface Transport and Fate Processes.* Lewis Publishers, USA.

Komnitsas, K; Kontopoulos, A; Lazar, I and Cambridge, M (1998) Risk assessment and proposed remedial actions in coastal tailings disposal sites in Romania. *Minerals Engineering*, **11** (12), 1179-1190.

Kontopoulos, A; Komnitsas, K; Xenidis, A and Papassiopi, N (1995) Environmental characterisation of the sulphidic tailings in Laviron. *Minerals Engineering*, **8**(10), 1209-1219.

Kundu, A; Saroha, AK and Nigam, KDP (2001) Liquid distribution studies in trickle-bed reactors. *Chemical Engineering Science,* **56**, 5963-5967.

Lapakko, K (2002) *Metal Mine Rock and Waste Characterisation Tools: An Overview*. MMSD (Mining, Minerals and Sustainable Development) Programme.

Lasaga, AC (1984) Chemical kinetics of water-rock interactions. *Journal of Geophysical Research,* **89**, 4009-4025.

Lawrence, DP (1997) The need for EIA theory-building. *Environmental Impact Assessment Review*, **17**, 79-107.

Lawrence, RW and Wang, Y (1996) *Determination of Neutralization Potential for Acid Rock Drainage Prediction,* MEND Report 1.16.3, Ottawa, Canada.

Lefebvre, R; Hockley, D; Smolensky, J and Gélinas, P (2001a) Multiphase transfer processes in waste rock piles producing acid mine drainage 1: Conceptual model and system characterisation. *Journal of Contaminant Hydrology,* **52**, 137-164.

Lefebvre, R; Hockley, D; Smolensky, J and Lamontagne, A (2001b) Multiphase transfer processes in waste rock piles producing acid mine drainage 2. Applications of numerical simulation. *Journal of Contaminant Hydrology,* **52**, 165-186.

Leinz, RW; Sutley, SJ; Desborough, GA and Briggs, PH (2000) An investigation of the partitioning of metals in mine wastes using sequential extractions. *Fifth International Conference on Acid Rock Drainage (ICARD 2000)* (pp. 1489-1499). Society for Mining, Metallurgy and Exploration, Denver.

Li, X and Thornton, I (2001) Chemical partitioning of trace and major elements in soils contaminated by mining and smelting activities. *Applied Geochemistry*, **16**, 1693-1706.

Lin, Z (1997) Mobilization and retention of heavy metals in mill-tailings from Garpenberg sulphide mines, Sweden. *The Science of the Total Environment*, **198**, 13-31.

Linklater, CM; Sinclair, DJ and Brown, PL (2005) Coupled chemistry and transport modelling of sulphidic waste rock dumps at the Aitik mine site, Sweden. *Applied Geochemistry*, **20**, 275-293.

Loos, MA; Cleghorn, C and Modinger, H (2000) Occurrence of bacteria causing acid mine drainage in the outer layers of coal waste dumps in relation to abiotic ecological determinants and soil covers used for dump rehabilitation. WRC Report Number 454/1/00. WRC, South Africa.

Mangold, DC and Tsang, C (1991) A summary of subsurface hydrological and hydrochemical models. *Reviews of Geophysics*, **29** (1), 51-79.

Marin, A et al. (2001) Development and validation of extraction methods for determination of zinc and arsenic speciation in soils using focused ultrasound: Application to heavy metal study in mud and soils. *Analytica Chimica Acta*, **442**, 305-318.

Mattigod, SV; Rai, D; Eary, LE and Ainsworth, CC (1990) Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: I. Review of the major elements. *J. Environ. Qual.*, **19**, 188-200.

McDonald, MG and Harbaugh, AW (1988) *MODFLOW: A modular three-dimensional finite-difference ground-water flow model.* United States Groundwater Service Scientific Publications Company, Washington.

McGregor, R and Blowes, DW (2002) The physical, chemical and mineralogical properties of three cemented layers within sulphide-bearing mine tailings. *Journal of Geochemical Exploration*, **76**, 195-207

Meadows, D (1998) Indicators and information systems for sustainable development. *A report to the Balaton group.* The Sustainable Institute, Hartland Four Corners, VT.

Meeussen, JCL (2003) ORCHESTRA: An object-orientated framework for implementing chemical equilibrium models. *Environmental Science and Technology*, **37**(6), 1175-1182.

Miller, SD; Jeffrey, JJ and Wong, JWC (1991) Use and misuse of the Acid-Base Accounting for "AMD" prediction. *Randol Gold Forum '91* (pp. 69-75). Randol International, Cairns.

Mills, C (1998) *Acid-Base Accounting (ABA) Test Procedures,* Enviromine (available online at http://www.environmine.com)

Mining Journal Editorial (1995) Metal of civilisation. *Mining Journal*, 325.

Mitchell, PB; Waller, CP and Atkinson, K (1994) Prediction of water contamination arising from disposal of solid wastes. *Hydrometallurgy '94*, Cambridge, England.

Mitchell, P (2000) Prediction, prevention, control and treatment of acid rock drainage. In A Warhurst and L Noronha (Ed.), *Environmental Policy in Mining: Corporate Strategy and Planning for Closure* (pp. 117-143). CRC Press.

Moore, JJ (1990) *Chemical Metallurgy*, Butterworth Heinemann.

Morera, MT; Echeverría, JC; Mazkiarán, C and Garrido, JJ (2001) Isotherms and sequential extraction procedures for evaluating sorption and distribution of heavy metals in soils. *Environmental Pollution*, **113**, 135-144.

Moskalyk, R and Alfantazi, A (2003) Review of copper pyrometallurgy practice: Today and tomorrow. *Minerals Engineering*, **16**, 893-919.

Mowat, FS and Bundy, KJ (2001) Correlation of field-measured toxicity with chemical concentration and pollutant availability. *Environment International*, **27**, 479-489.

Murr, L; Schlitt, W and Catheles, L (1981) Experimental observations of solution flow in leaching of copper-bearing waste. *2nd SME-SPE International Solution Mining Symposium*. Denver. 271.

MMSD (Mining, Minerals and Sustainable Development) Project (2002) Mining for the future*. Appendix A: Large Volume Waste Working Paper*. No 31.

Moncur, MC; Ptacek, CJ; Blowes, DW and Jambor, JL (2005) Release, transport and attenuation of metals from an old tailings impoundment. *Applied Geochemistry,* **20**, 639-659.

Morin, KA; Cherry, JA; Davé, NK; Lim, TP and Vivyurak, AJ (1988) Migration of acidic groundwater seepage from uranium-tailings impoundments. I. Field study and conceptual hydrogeochemical model. *J Contam. Hydrol.,* **2**, 271-303.

Mwale, AH; Musonge, P and Fraser, DM (2005) The influence of particle size on energy consumption and water recovery in comminution and dewatering systems. *Minerals Engineering*, **18**, 915-926.

Ng'andu, DE (2001) The effect of underground mine water on performance of the Mufilira flotation process. *The Journal of the South African Institute of Mining and Metallurgy*, 367-380.

Nigam, KDP; Iliuta, I and Larachi, F (2002) Liquid back-mixing and mass transfer effects in trickle-bed reactors filled with porous catalyst particles. *Chemical Engineering and Processing,* **41**, 365-379.

Niggli, P (1954) *Rocks and Mineral Deposits*. W H Freeman and Co, San Francisco.

Noble, BF (2000) Strengthening EIA through adaptive management: a systems perspective. *Environmental Impact Assessment Review*, **20**, 97-111.

Noble, BF (2002) The Canadian experience with SEA and sustainability. *Environmental Impact Assessment Review*, **22**, 3-16.

Notten, PJ (2001) Life cycle inventory uncertainty in resource-based industries- A focus on coal-based power generation. *PhD thesis dissertation,* University of Cape Town, South Africa.

OECD Waste Management Policy Group (1993) *Study on Nationally Designated Hazardous Waste Characteristics and Corresponding Test Procedures in OECD Countries*. Draft Document, ENV/EPOC/WMP (93) 6.

OLI Systems Inc (1991) *Aqueous Systems Modeling Course and Workshop*. Course notes.

Outokumpu (2002). Outokumpu HSC chemistry for windows. *User's Guide,* Version 5.1. Outokumpu Research Oy, Finland.

Paktunc, AD (1999) Mineralogical constraints on the determination of neutralization potential and prediction of acid mine drainage. *Environmental Geology*, **39**, 103-111.

Parametrix, I (1995) Persistence, bioaccumulation and toxicity of metals and metal compounds. *International Council on Metals and the Environment* .

Parkhurst, DL (1995) User's guide to PHREEQC- A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations. *US Geological Survey Water-Resources Investigations Report 95-4227.*

Partidario, MR (2000) Elements of an SEA framework-improving the added value of SEA. *Environmental Impact Assessment Review*, **20**, 647-663.

Patinha, C; da Silva, EF and Fonseca, EC (2004) Mobilisation of arsenic at the Talhadas old mining area-Central Portugal. *Journal of Geochemical Exploration*, **84**, 167-180.

Pennington, DW and Yue, PI (2000) Options for the comparison of process design alternatives in the context of regional toxicological impacts. *Journal of Cleaner Production*, **8**, 1-9.

Pesic, B; Oliver, DJ; and Wichlacz, P (1989) An electrochemical method of measuring the oxidation rate of ferrous to ferric iron with oxygen in the presence of Thiobacillus Ferrooxidans. *Biotechnology and Bioengineering*, **33**, 428-439.

Petersen, J (1998) Assessment and modelling of chromium release in minerals processing waste deposits. *PhD thesis dissertation,* University of Cape Town, South Africa.

Petersen, J; Stewart, M and Petrie, J (2000) Management of ferro-alloy wastes. In A Warhurst and L Noronha (Eds.), *Environmental Policy in Mining: Corporate Strategy and Planning for Closure* (pp. 217-228). CRC Press.

Petruk, W and Schnarr, J (1981) The behaviour of galena, chalcopyrite and tetrahedrite during flotation of a fine-grained base metal ore in the concentrate of Brunswick Mining and Smelting Limited. In D Hausen and W Park (Ed.), *Process Mineralogy: Extractive Metallurgy, Mineral Exploration, Energy Resources* (pp. 201-212). The Metallurgical Society of AIME.

PSE (2002) *gPROMS introductory user guide*. Process Systems Enterprise Ltd., London.

Ptacek, CJ and Blowes, DW (2003) Geochemistry of concentrated waters and mine-waste sites. In. JL Jambor, DW Blowes and AIM Ritchie (Ed.), *Environmental Aspects of Mine Wastes: Short Course Series 31*. Mineralogical society of Canada, 239-252.

Ribet, I; Ptacek, CJ; Blowes, DW and Jambor, JL (1995) The potential for metal release by reactive dissolution of weathered mine tailings. *Journal of Contaminant Hydrology*, **17**, 239-273.

Ripley, EA; Redmann, RE and Crowder, AA (1996) *Environmental Effects of Mining.* St Lucie Press.

Roberts, EJ; Stavenger, PL; Bowersox, JP, Walton; AK and Mehta, M (1971) Solid/Solid separations. *Chemical Engineering, Deskbook issue*, 89-98.

Romano, CG; Mayer, KU; Jones, DR; Ellerbroek, DA and Blowes, DW (2003) Effectiveness of various cover scenarios on the rate of sulphide oxidation of mine tailings. *Journal of Hydrology*, **271**, 171-187.

Rosenqvist, T (1983) *Principles of Extractive Metallurgy*. McGraw-Hill Book Company.

Rubenstein, J and Barsky, L (2002) *Non-Ferrous Metal Ores: Deposits, Minerals and Plants.* Taylor & Francis.

Sassoon, M (2000) Effective environmental impact assessment. In A Warhurst and L Noronha (Eds.), *Environmental Policy in Mining: Corporate Strategy and Planning for Closure* (pp. 101-116). CRC Press.

Seal, R and Foley, N (2002) *US Geological Survey: Progress on Geoenvironmental Models for Selected Mineral Deposit Types*. United States Bureau of Mines.

SETAC (Society of Environmental Toxicology and Chemistry) (1998) Life cycle impact assessment: the state of the art. *Report of the SETAC Life-Cycle Assessment (LCA) Impact Assessment Workgroup.*

Singer, PC and Stumm, W (1970) Acidic mine drainage: The rate-determining step. *Science,* **167**, 1121-1123.

Skousen, J; Simmons, L; McDonald, LM and Ziemkiewicz, P (2000) Acid-base accounting to predict post-mining drainage quality on surface mines. *J. Environ. Qual*., **31**, 2034-2044.

Sobek, AA; Schuller, WA; Freeman, JR and Smith, RM (1978) *Field and Laboratory Methods Applicable to Overburden and Minesoils.* US EPA.

Sondag, F (1981) Selective extraction procedures applied to geochemical prospecting in an area contaminated by old mine workings. *Journal of Geochemical Exploration*, **15**, 645–652.

Steefel, CI and Lasaga, AC (1994) A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with applications to reactive flow in single phase hydrothermal system. *American Journal of Science,* **294**, 529-592.

Stegemann, JA and Cote, PL (1990) *Investigation of Tests Methods for Solidified Waste Evaluation-A Cooperative Program.* Environment Canada Conservation and Protection Wastewater Technology Centre.

Stewart, M. (1999) *Environmental Decision-Making in Minerals Processing Design*. PhD dissertation thesis, Department of Chemical Engineering, University of Cape Town, South Africa.

Stewart, M (2001) The application of life cycle assessment to mining, minerals and metals. *MMSD Life Cycle Assessment Workshop Report*. Sydney.

Stewart, M; Guirco, D and Petrie, JG (2003) A sustainability analysis of the metals value chain: A focus on copper. In L Lorenzen and D Bradshaw (Ed.), *XXII International Mineral Processing Congress Proceedings* (pp. 572-582). University of Cape Town, Cape Town.

Stewart, M and Petrie, J (2006) A process systems approach to life cycle inventories for minerals: South African and Australian case studies. *Journal of Cleaner Production*, **1**, 1042-1056.

Strőmberg, B and Banwart, SA (1999) Experimental study of acidity-consuming processes in mining waste rock: Some influences of mineralogy and particle size. *Applied Geochemistry*, **14**, 1-16.

Stumm, W and Morgan, JJ (1981) Aquatic chemistry: An introduction emphasizing chemical equilibria in natural waters, John Wiley & Sons, New York.

Sutherland, RA (2002) Comparison between non-residual Al, Co, Cu, Fe, Mn , Ni, Pb and Zn released by a three-step sequential extraction procedure and a dilute hydrochloric acid leach for soil and road deposited material. *Applied Geochemistry*, **17**, 353-365.

Tessier, A and Campbell, PGC and Bisson, M (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, **51**, 844-851.

Thornton, I (1983) *Applied Environmental Geochemistry*. Academic Press.

Trans, AB; Miller, S; Williams, DJ; Fines and Wilson, GW (2003) Geochemical and mineralogical characterisation of two contrasting waste rock dumps. *The INAP Waste Rock Dump Characterisation Project.* Cairns, QLD, 939 -947.

Tukker, A (2000) Life cycle assessment as a tool in environmental impact assessment. *Environmental Impact Assessment Review*, **20**, 435-440.

Twardowska, I and Szczepanska, J (2002) Solid waste: Terminological and long-term environmental risk assessment problems exemplified in a power plant fly ash study. *The Science of the Total Environment*, **285**, 29-51.

UNIDO (United Nations Industrial Development Organisation) (1987) Environmental assessment and management in the production of six non-ferrous metals: Aluminium, nickel, copper, lead, zinc and tin, *Sectorial Studies Series No 30.*

US EPA (United States Environmental Protection Agency) (1986). *Primary Copper Smelting Section 12: Compilation of Air Pollutant Emission Factors*.

US EPA (United States Environmental Protection Agency) (1989) Risk assessment guidance for superfund: Environmental evaluation manual. *OSWER Directive 9285.7-01*, EPA/530-SW-011B. US Government Printing Office, Washington DC.

US EPA (United States Environmental Protection Agency) (1994) *Acid Mine Drainage Prediction*.

Usher, BH; Cruywagen, L-M; de Necker, E and Hodgson, FDI (2003a) On-site laboratory investigations of spoil in opencast collieries and the development of acid-base accounting procedures. *WRC Report Number 1055/1/03.* WRC, South Africa.

Usher, BH; Cruywagen, L-M; de Necker, E and Hodgson, FDI (2003b) Acid-base: Accounting, techniques and evaluation (ABATE). *WRC Report Number 1055/2/03.* WRC, South Africa.

Van der Heijde, PKM and Elnawawy, OA (1993) *Compilation of ground-water models*, EPA Report 600-R-93-118, International Ground Water Modelling Centre, US Environmental Protection Agency, Golden, CO.

Van der Sloot, HA and Dijkstra, JJ (2004) Development of horizontally standardized leaching tests or construction materials: a material based or release based approach? In *Industrial Leaching Mechanisms for Different Materials*. Energy Research Centre of the Netherlands (ECN).

Van der Sloot, H; Meeussen, H; Kosson, DS and Sanchez, F (2003a) An overview of leaching assessment for waste disposal and materials use. *WASCON 2003*, San Sebastian.

Van der Sloot, HA; van Zomeren, A; Seignette, P; Dijkstra, J; Comans, RNJ; Meeussen, H; Kosson, DS and Hjelmar, O (2003b) Evaluation of environmental aspects of alternative materials using an integrated approach assisted by a database/expert system. *Advances in Waste Management and Recycling*, Dundee.

Van Herck, P and Vandecasteele, C (2001) Evaluation of the use of a sequential extraction procedure for the characterization and treatment of metal containing solid waste. *Waste Management*, **21**, 685-694.

Van Huyssteen, E (1998) The relationship between mine process tailings mineralogy and pore water composition. In: W. Petruk (ed). *Waste Characterisation and Treatment*. Society for Mining, Metallurgy and Exploration, INC, 91-108.

Van Zyl, D (1993) Mine waste disposal. In DE Daniel (Ed), *Geotechnical Practice for Waste Disposal,* Chapter 12 (pp. 269-286). Chapman and Hall, London.

Wahlstrőm, M (1996) Nordic recommendation for leaching tests for granular waste materials. *The Science of the Total Environment*, **178**, 95-102.

Warhurst, A (2000) Mining, mineral processing and extractive metallurgy: An overview of the technologies and their impact on the physical environment. In A Warhurst and L Noronha (Ed.), *Environmental Policy in Mining: Corporate Strategy and Planning for Closure* (pp. 33-56). CRC Press.

Warhurst, A and Noronha, L (2000) Integrated environmental management through planning for closure from the outset: The challenges. In A Warhurst and L Noronha (Ed.), *Environmental Policy in Mining: Corporate Strategy and Planning for Closure* (pp. 13-32). CRC Press.

Wates JA; Lorentz, SA; Marais, H; Baxter, BJM; Theron, M and Dollar, L (2006) An evaluation of the performance and effectiveness of improved soil cover designs to limit through-flow of water and ingree of air. *WRC Report Number 1350/1/06.* WRC, South Africa.

Weber, PA; Thomas, JE; Skinner, WM; and Smart, RSC (2004a) Improved acid neutralisation capacity assessment of iron carbonates by titration and theoretical calculation. *Applied Geochemistry*, **19**, 687-694.

Weber, PA; Thomas, JE; Skinner, WM and Smart, RSC (2004b) Geochemical effects of oxidation products and frambiodal pyrite oxidation in acid mine drainage prediction techniques. *Applied Geochemistry*, **19**, 1953-1974.

White, WW; Lapakko, KA and Cox, RL (1999) Static-test methods commonly used to predict acid-mine drainage: practical guidelines for use and interpretation. In *The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues* (pp 3255-3338). Society of Economic Geologists, Chelsea, MI.

Wenzel, H (1999) Life cycle assessment in pollution prevention. In SK Sikdar and Diweker (Ed.), *Tools and Methods for Pollution Prevention (*pp. 119-129). Kluwer Academic Publishers.

Wiertz, J (2005) University of Chile, Private communications.

Wills, B (1997) *Mineral Processing Technology*. Butterworth-Heinemannn.

Wunderly, MD; Blowes, DW; Frind, EO and Ptacek, CJ (1996) Sulfide mineral oxidation and subsequent reactive transport of oxidation products in mine tailings impoundments: A numerical model. *Water Resources Research,* **32** (10), 3173-3187.

Yeh, G-T and Tripathi, VS (1989) A critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components. *Water Resources Research,* **25** (1), 93-108.

Zheng, C (1992) *MT3D: A Modular Three-Dimensional Transport Model for Simulation of Advection, Dispersion and Chemical Reactions of Contaminants in Groundwater Systems.* S.S. Papadopoulos & Associates, Inc, Maryland, USA.

Zheng, C and Bennett, GD (1995) *Applied Contaminant Transport Modelling: Theory and practice.* Van Nostrand Reinhold, New York.

APPENDIX A

SOUTH AFRICAN MINERAL WASTE INVENTORY: PROCESS FLOWSHEETS AND DATA ASSESSMENT FOR THE VARIOUS INDUSTRY SECTORS

What follows are the generalised industry sector flowsheets and summary of the availability and quality of the data collated within the existing inventory database. The full inventory, in spreadsheet format, can be found on the CD that accompanies this document (Microsoft Excel).

The process flowsheets included below detail all major technologies and unit operations in place within the various sub-sectors. The tables in this section not only highlight data gaps, but also evaluate the quality of the data by means of the following simple ranking system:

✓	Denotes poor quality or limited data or low confidence in values
✓✓	Denotes acceptable data quality providing basic information
✓✓✓	Denotes good quality data providing detailed information.

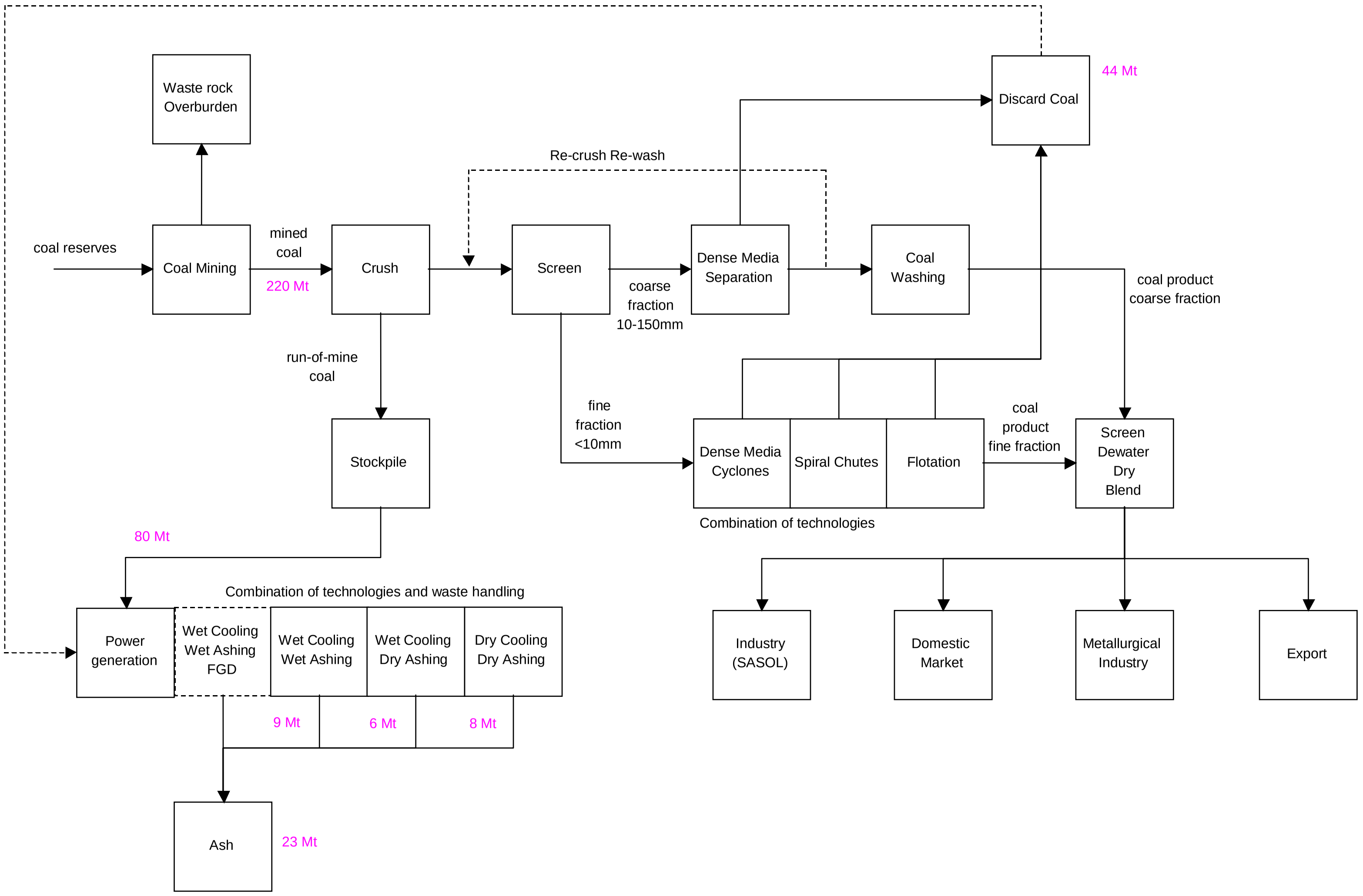
Coal Sector

Generalised flowsheet for the coal sector

There are two possible process routes for mined coal. Run of mine (ROM) coal is either sent directly to power generation or processed, using a variety of technologies, to produce a coal with specified ash and sulphur contents for export and local industry needs. The solid waste streams from these processes include waste rock or overburden from mining, discard coal from coal beneficiation processes and ash from power generation. The process flowsheet also identifies coal stockpiles, on both the mine site and the power generation site, as a solid waste. This is because these temporary stockpiles give rise to impacts similar to those typically associated with solid wastes.

Data gaps and quality

The waste inventory for the coal sub-sector is at present the most comprehensive and has minimal data gaps. This can be attributed to previous data collection efforts to support predictive modelling work undertaken by Notten (2001) and Hansen (2004). Data collected is also of a high quality. As with other industry sub-sectors, there is little information on coal-bearing ores and mining techniques. The method of mining in particular will have a bearing on both material management (mined ore and waste rock) and water management. Further, different mining techniques can lead to substantially different environmental considerations. Subsidence and flooded underground workings, for example, are two issues associated with underground mining. Technical information regarding waste management of discard deposits is currently lacking. Such technical information includes: typical disposal practice, average dimensions, level of compaction etc. Similar information is required for coal stockpiles with the average life of the stockpile before reclamation being an additional factor of interest.


coal reserves
Coal Mining
Waste rock Overburden
mined coal
220 Mt
Crush
run-of-mine coal
Stockpile
80 Mt
Re-crush Re-wash
Screen
coarse fraction 10-150mm
fine fraction <10mm
Dense Media Separation
Coal Washing
Discard Coal
44 Mt
Dense Media Cyclones
Spiral Chutes
Flotation
Combination of technologies
coal product fine fraction
coal product coarse fraction
Screen Dewater Dry Blend
Industry (SASOL)
Domestic Market
Metallurgical Industry
Export
Combination of technologies and waste handling
Power generation
Wet Cooling Wet Ashing FGD
Wet Cooling Wet Ashing
Wet Cooling Dry Ashing
Dry Cooling Dry Ashing
9 Mt
6 Mt
8 Mt
Ash
23 Mt

Data gaps and quality for the coal sector

Data requirement	Waste rock	Discard coal	Coal stockpile	Ash from power generation[1]		
				dry-dry	wet-dry	wet-wet
Waste properties (qualitative)		✓✓		✓✓	✓✓	✓✓
Environmental issues		✓✓✓	✓✓	✓✓	✓✓	✓✓
Process information						
- Production volumes		✓✓		✓✓✓	✓✓✓	✓✓✓
- S:L ratio		✓✓		✓✓✓	✓✓✓	✓✓✓
- Particle size distribution		✓✓				
Waste management						
- Deposit area				✓✓✓	✓✓✓	✓✓✓
- Technical information				✓✓✓	✓✓✓	✓✓✓
- Other information		✓		✓✓✓[2]	✓✓✓[2]	✓✓✓[2]
Waste characterisation						
- Components/Mineralogy		✓		✓✓✓	✓✓✓	✓✓✓
Liquid volumes co-disposed						
- Volume effluent		✓✓		✓✓✓	✓✓✓	✓✓✓
- Quality of effluent				✓✓✓	✓✓✓	✓✓✓
Leachability studies			✓✓✓[3]		✓✓✓[4]	✓✓✓[5]

[1] Information derived from Pippa Notten's power station inventory model

[2] Data obtained from various Eskom reports

[3] Sequential extraction tests performed on Lethabo coal - data generated by UCT

[4] Sequential extraction tests performed on Lethabo ash - data generated by UCT

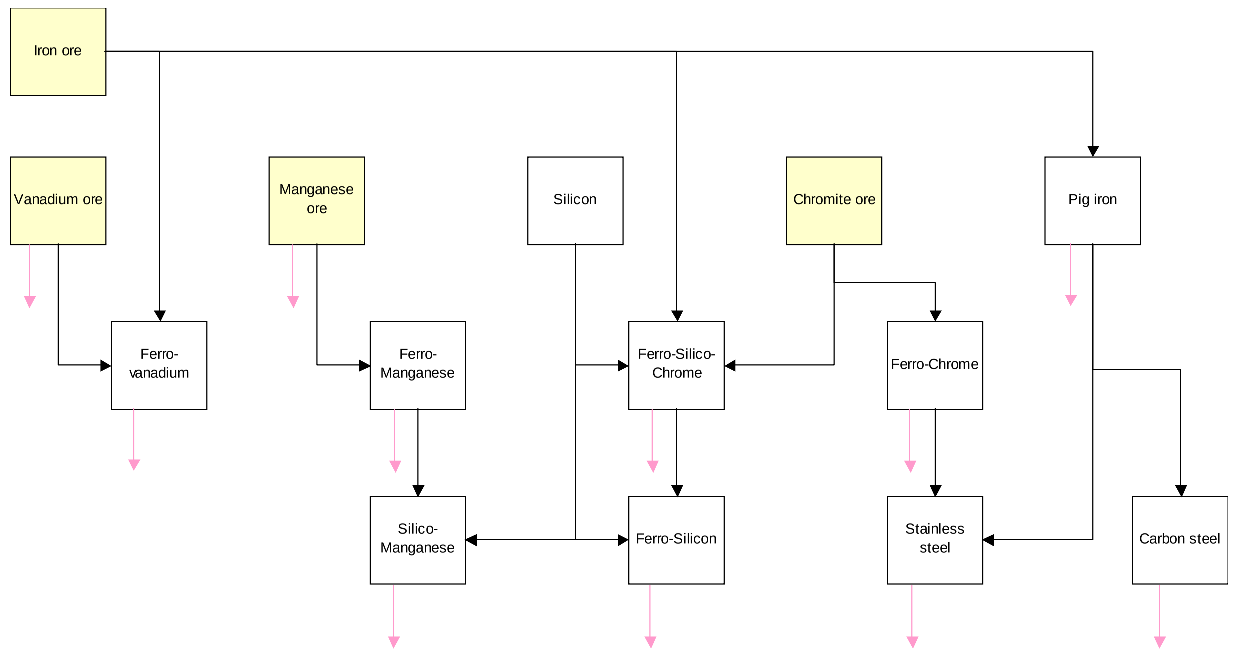
[5] Sequential extraction tests performed on Duvha ash - data generated by UCT; Other leachability studies from report by F. Hodgson

Ferro-Alloys Sector

Generalised process flowsheets

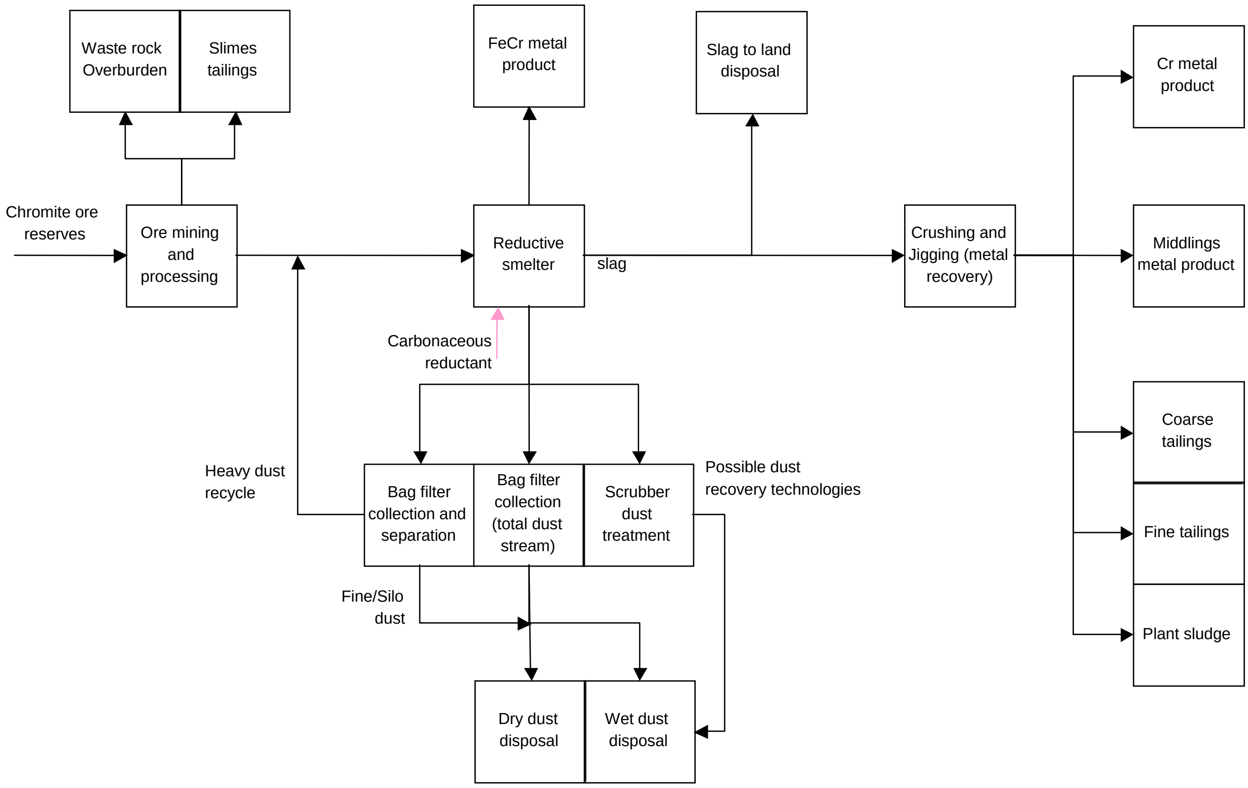
The ferro-alloys industry sector is complex and characterised by an integrated network of mining, ore production and processing, resulting in a number of intermediate products that are either exported or become inputs to downstream processes. This sector also produces a wide array of wastes at all process levels, with a significant portion of these wastes having the potential to be either recycled or processed to recover metal value. To simplify this industry sector, only the process routes that lead to the production of ferrochrome, ferrovanadium, ferromanganese and stainless steel are considered here.

Overview of the entire ferro-alloys sector:



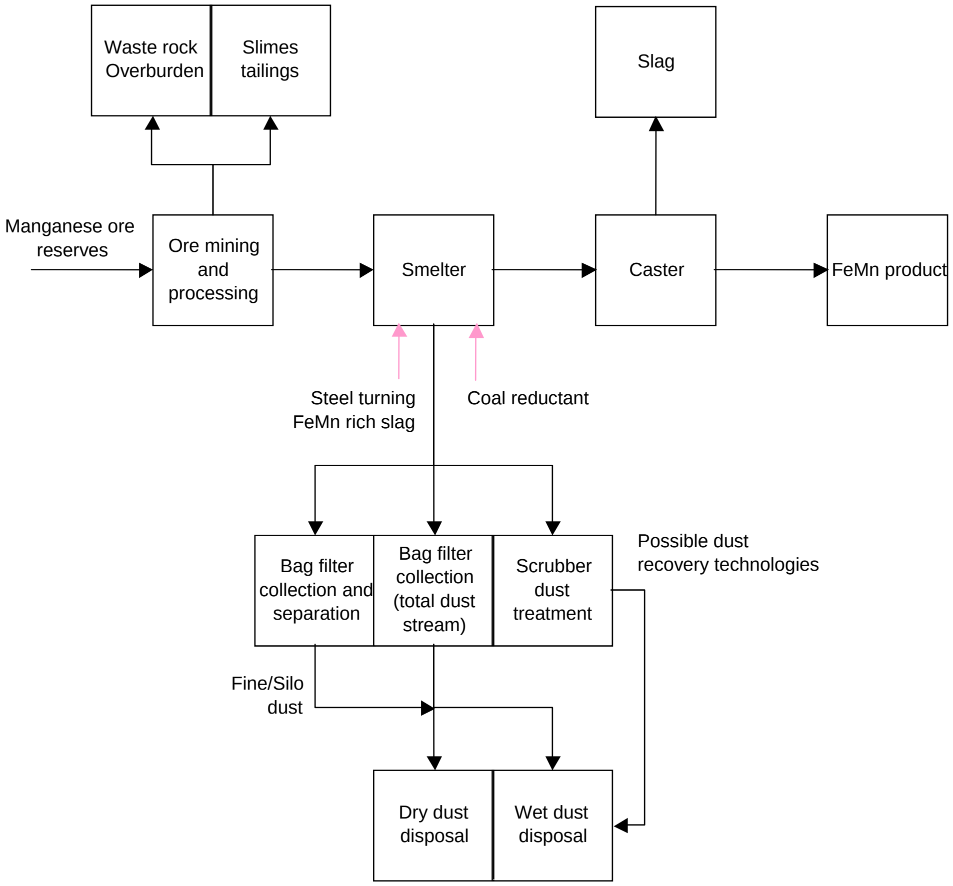
Ferrochrome process flowsheet:

In this industry, mined ore is sent to a reductive smelter that gives rise to two solid waste streams: a waste slag and smelter dust. Recently metal recovery technology has become available and some plants process the slag, through crushing and jigging, to extract the residual metal value. The resulting tailings are then sent to land disposal. Waste management options for the dust include collection and separation using bag filters. Separation of the dust into a coarse and fine fraction allows the heavier fraction to be recycled to the smelter. Alternatively, wet scrubbers may be used to collect the dust and the resulting scrubber sludge is sent to landfill. Slags and dusts have historically been co-disposed



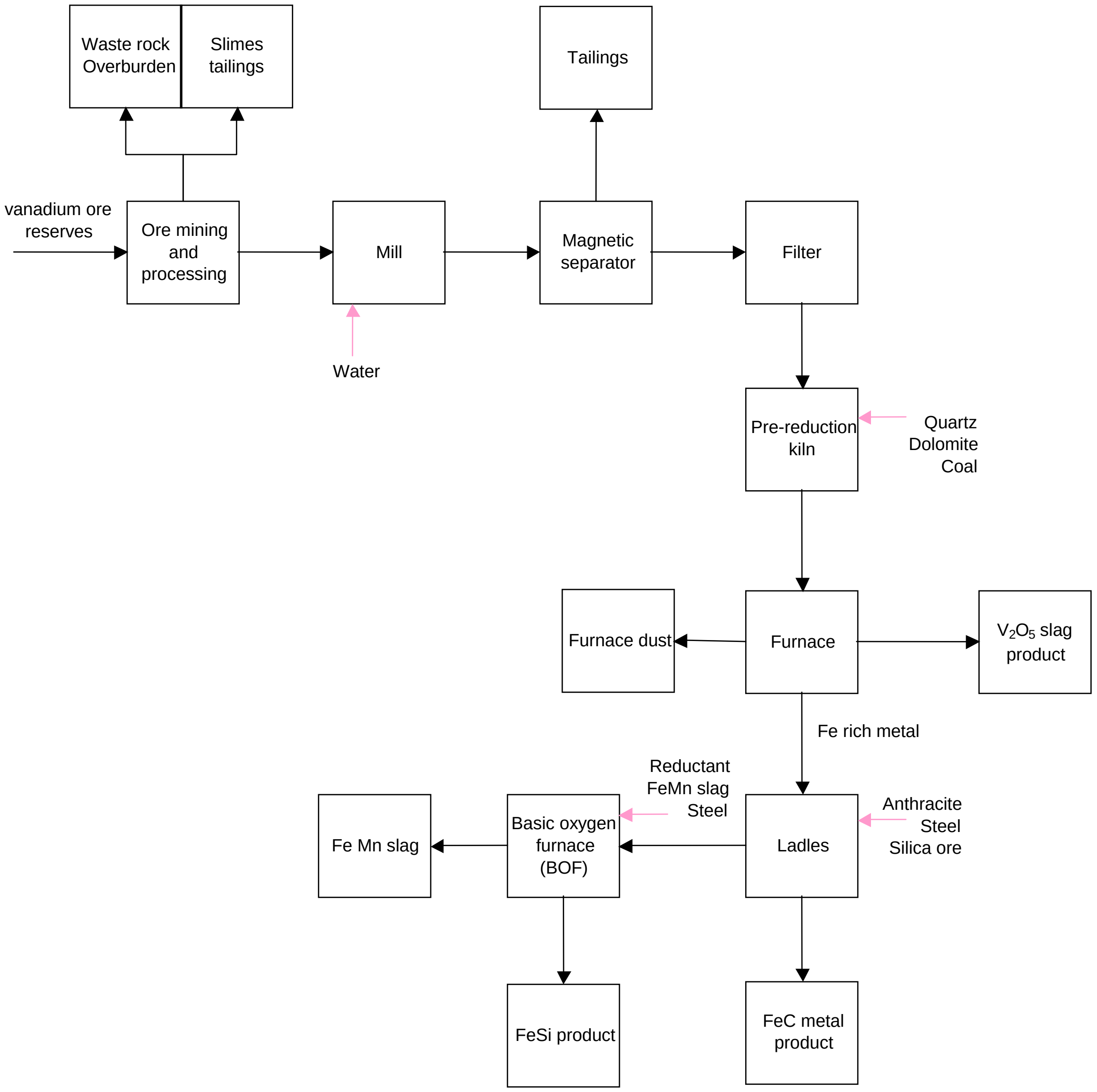
Ferromanganese process flowsheet:

The ferromanganese process flowsheet is very similar to the ferrochromium flowsheet but without the option of metal recovery from the waste slag. Similarly to the production of ferrochrome, solid wastes produced comprise slag from casting and dust from smelting.

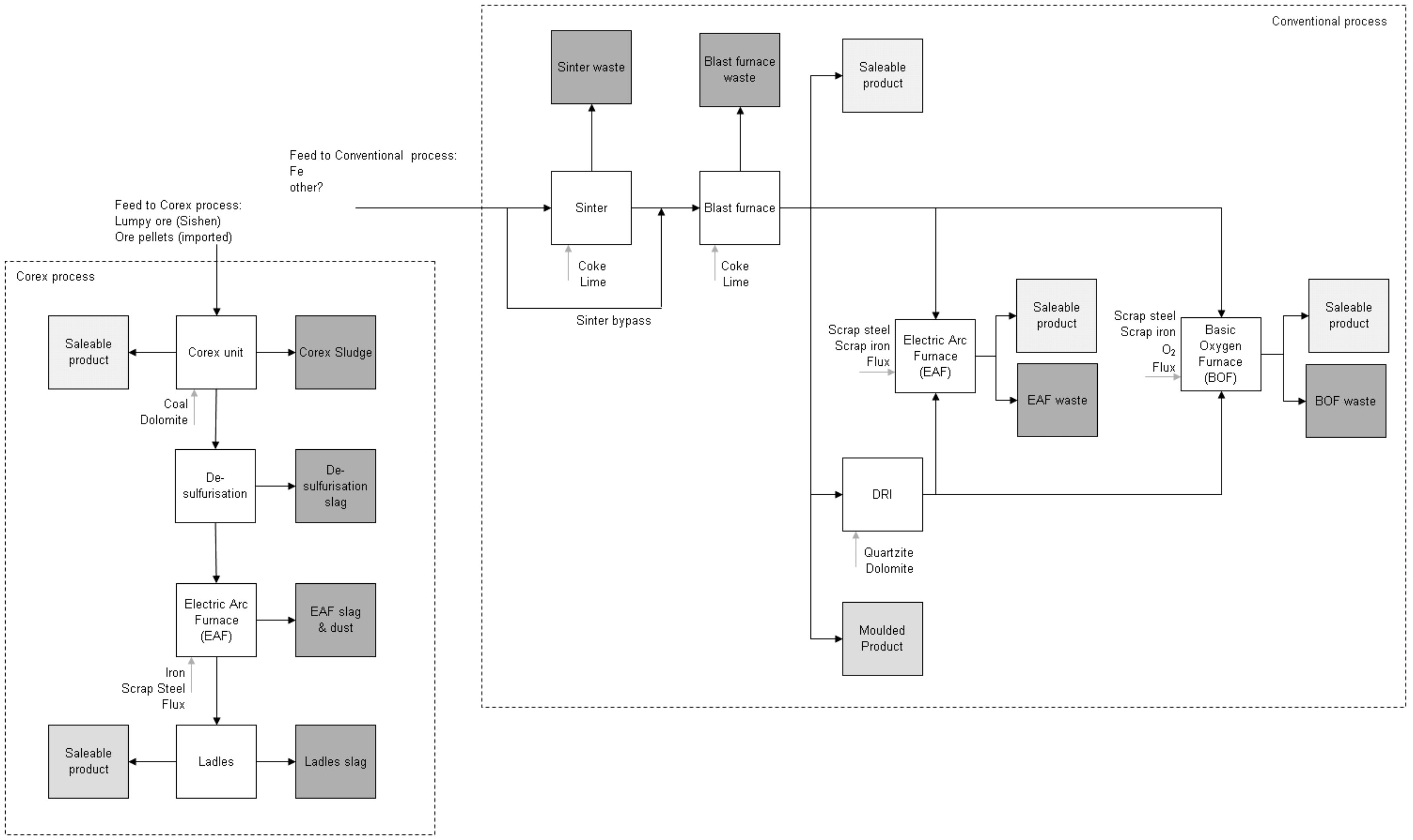


Ferrovanadium process flowsheet

The solid wastes arising from the production of ferrovanadium include tailings from magnetic separation, furnace dust from the furnace that produces the vanadium slag product, and a ferromanganese slag from the basic oxygen furnace (BOF).



Stainless Steel process flowsheet:



Data gaps and quality

There is little information available on the characteristics and management of ores. Only one confidential report was sourced that contained ore particle size distribution and detailed characterisation data for two ferro-manganese ores (namely, a Mamatwan-type ore and a Hotazel-type ore). No information is available for any other ore body. There is also limited data available regarding the production and characteristics of waste rock and tailings from concentration activities for the ferro-alloy sector. Again, there is little information on waste management for all wastes arising from this industry sub-sector. In addition, production figures for ferrochrome wastes are missing. Efforts to source these figures have been unsuccessful.

Data gaps: ores from ferro-alloy sub-sector

Data requirement	Iron ore	Chromite ore	Manganese ore[1]	Vanadium ores
Ore properties (qualitative)				
Environmental issues				
Process information - Mined volumes - S:L ratio - Particle size distribution			✓✓✓	
Ore management - Technical information - Other information				
Ore characterisation - Components/Mineralogy			✓✓✓	

[1] Ore particle size distribution and detailed characterisation data available for two ferro-manganese ores (Mamatwan- type ore and Hotazel-type ore)

Data gaps: wastes from production of ferrovanadium

Data requirement	Waste rock overburden	Thickener slimes	Magnetic sep. waste	Furnace dust	FeMn slag
Waste properties (qualitative)					
Environmental issues	✓				✓
Process information - Production volumes - S:L ratio - Particle size distribution			✓✓ ✓	✓✓	✓✓
Waste management - Deposit area - Technical information - Other information					
Waste characterisation - Components/Mineralogy			✓✓	✓✓	✓✓
Liquid volumes co-disposed - Volume effluent - Quality of effluent			✓✓		
Leachability studies					

Data gaps: wastes from production of ferromanganese

Data requirement	Waste rock overburden	Thickener slimes	Bag filter dust	Scrubber sludge
Waste properties (qualitative)				
Environmental issues	✓		✓	✓
Process information - Production volumes - S:L ratio - Particle size distribution			✓✓	
Waste management - Deposit area - Technical information - Other information				
Waste characterisation - Components/Mineralogy			✓✓✓[1]	
Liquid volumes co-disposed - Volume effluent - Quality of effluent				
Leachability studies				

[1] Waste characterisation data from confidential report

Data gaps: wastes from production of ferrochrome

Data requirement	Waste rock	Tailings slimes	LCFeCr slag	HCFeCr slag	ICFeCr slag	LCFeCr dust	HCFeCr dust	ICFeCr dust	Metal recovery tailings
Waste properties (qualitative)									
Environmental issues	✓		✓	✓	✓	✓	✓	✓	✓
Process information - Production volumes - S:L ratio - Particle size distribution						✓[1]	✓[1]	✓[1]	
Waste management - Deposit area - Technical information - Other									
Waste characterisation			✓✓✓[2]	✓✓✓[2]	✓✓[2]	✓✓✓[2]	✓✓✓[2]	✓✓[2]	
Liquid volumes co-disposed - Volume effluent - Effluent quality							✓[2]	✓[2]	
Leachability studies									

[1] Estimate of total ferro-chrome dust stream – private communications with JL Broadhurst

[2] Waste characterisation data from confidential reports

Data gaps: wastes from production of ferrosilicon and silicomanganese

Data requirement	Fe-Si		Si-Mn	
	FeSi slag	FeSi dust	SiMn slag	SiMn dust
Waste properties (qualitative)				
Environmental issues				
Process information - Production volumes - S:L ratio - Particle size distribution	✓✓	✓✓	✓✓	✓✓
Waste management - Deposit area - Technical information - Other information				
Waste characterisation - Components/Mineralogy	✓✓	✓✓	✓✓	✓✓
Liquid volumes co-disposed - Volume effluent - Quality of effluent				
Leachability studies				

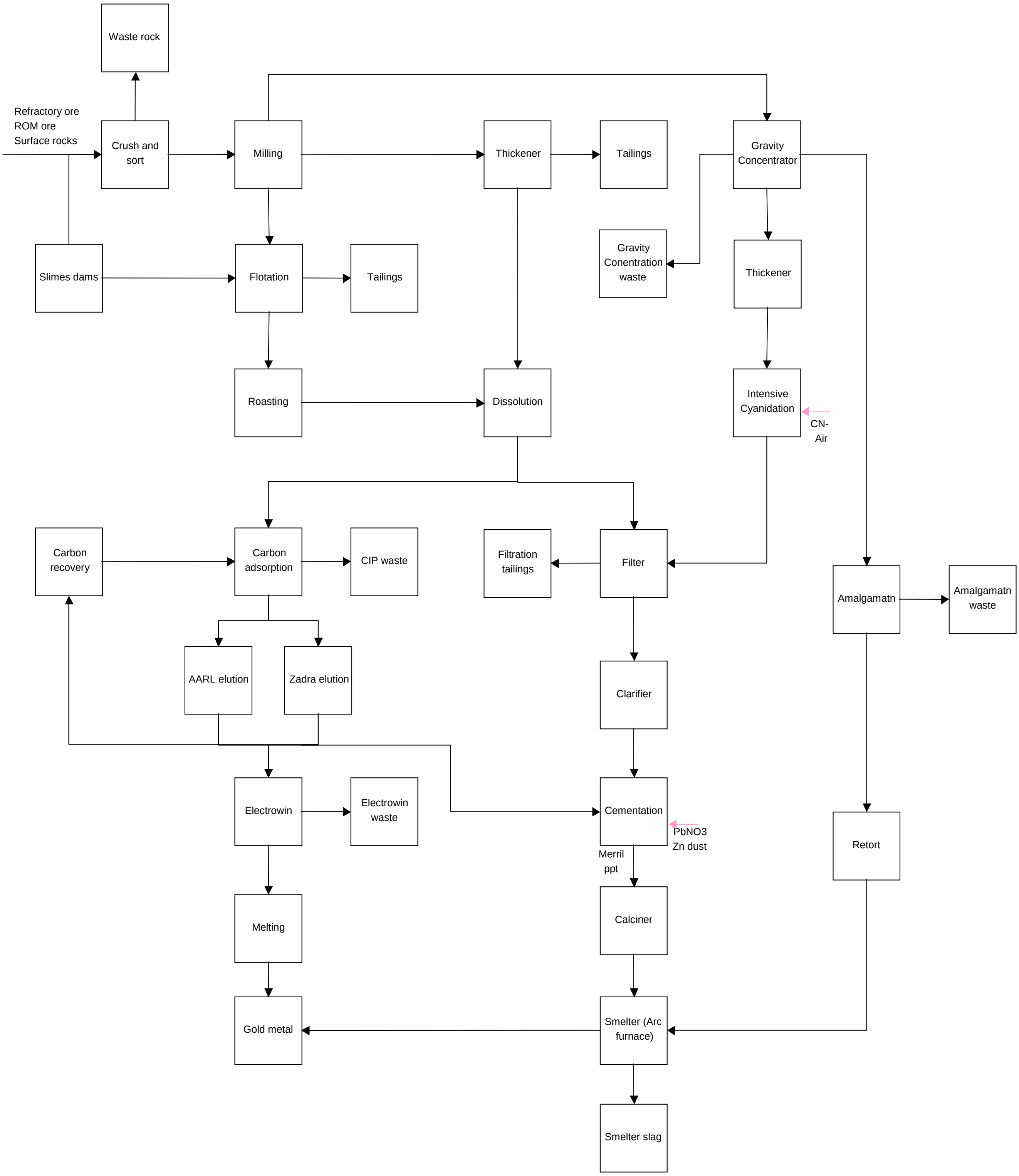
Data gaps: wastes from production of stainless steel

Data requirement	Corex process					Conventional process			
	Corex sludge	Desulph. slag	EAF slag	EAF dust	Ladles slag	Sinter waste	Blast furnace waste	EAF waste	BOF waste
Waste properties (qualitative)									
Environmental issues									
Process information - Production volumes - S:L ratio - Particle size distribution	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓
Waste management - Deposit area - Technical information - Other information									
Waste characterisation - Components/Mineralogy	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓
Liquid volumes co-disposed - Volume effluent - Quality of effluent									
Leachability studies									

Gold Sector

Generalised process flowsheet for the gold sector

Gold is produced in South Africa using three different process routes. Gravity concentration followed by mercury amalgamation is the oldest technology and yields the lowest gold recoveries. This technology has been largely superseded by technologies based on cyanide dissolution. Within the cyanide dissolution based processes, older processes follow dissolution with filtration and subsequent cementation of gold from solution. More recently, semi-batch carbon-in-pulp or CIP adsorption has replaced clarification and cementation processes. Some plants may employ gravity concentration after comminution. Interestingly, the reclamation of tailings or mine dump sands accounts for approximately 43% of ore processed (Stewart, 1999).



Data gaps and quality

As with other industry sectors, waste management data is lacking. In addition, waste characterisation data in terms of waste components and/or mineralogy needs to be sourced.

Data gaps for the gold sector

Data requirement	Waste rock	Flotation tailings	Thickener tailings	Filtration tailings	CIP waste	Electro-winning waste	Smelter slag	Amalga-mation waste	Gravity conc. waste
Waste properties (qualitative)									
Environmental issues	✓	✓	✓	✓	✓		✓	✓	✓
Process information									
- Production volumes	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓
- S:L ratio	n/a	✓✓	✓✓	✓✓	✓✓	n/a	n/a	✓✓	✓✓
- Particle size distribution									
Waste management									
- Deposit area									
- Technical information									
- Other information									
Waste characterisation						✓	✓		
Liquid volumes co-disposed									
- Volume effluent	n/a	✓✓	✓✓	✓✓	✓✓	n/a	n/a	✓✓	✓✓
- Quality of effluent	n/a			✓[1]	✓[1]	n/a	n/a		
Leachability studies									

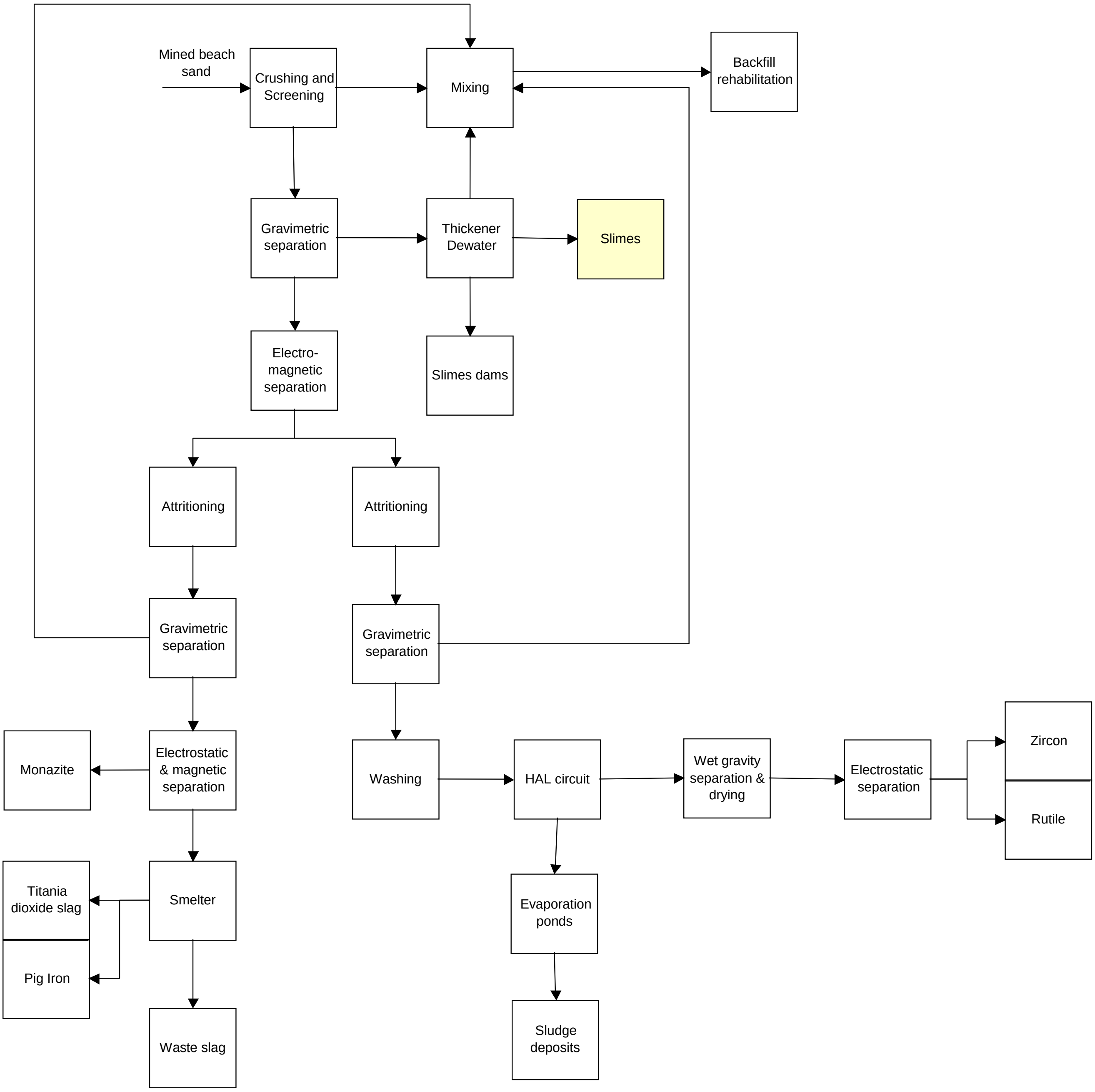
[1] TDS only

n/a refers to data requirements that are not applicable to the waste stream

Mineral Sands Sector

Generalised process flowsheet for the mineral sands sector

This process involves the physical concentration of the titanium-rich sand and subsequent pyrometallurgical processing of this concentrate. A large proportion of the solid waste generated from this process is sand, which is used as backfill and returned to the mine workings. In addition, sludge deposits arise from the HAL (hydrochloric acid leach) circuit and a waste slag from smelting.


Mined beach sand
Crushing and Screening
Mixing
Backfill rehabilitation
Gravimetric separation
Thickener Dewater
Slimes
Electro-magnetic separation
Slimes dams
Attritioning
Attritioning
Gravimetric separation
Gravimetric separation
Monazite
Electrostatic & magnetic separation
Washing
HAL circuit
Wet gravity separation & drying
Electrostatic separation
Zircon
Rutile
Titania dioxide slag
Smelter
Pig Iron
Evaporation ponds
Waste slag
Sludge deposits

Data gaps and quality

Due to the confidentiality surrounding this industry sub-sector, the mineral sands waste inventory is largely incomplete.

Data gaps for the mineral sands sector

Data requirement	Slimes from thickening	Smelter slag	Slimes from HAL circuit
Waste properties (qualitative)			
Environmental issues	✓	✓	✓
Process information - Production volumes - S:L ratio - Particle size distribution	✓[1]	✓[1]	✓[1]
Waste management - Deposit area - Technical information - Other information			
Waste characterisation - Components/Mineralogy			
Liquid volumes co-disposed - Volume effluent - Quality of effluent	✓[2]	✓[2]	✓[2]
Leachability studies			

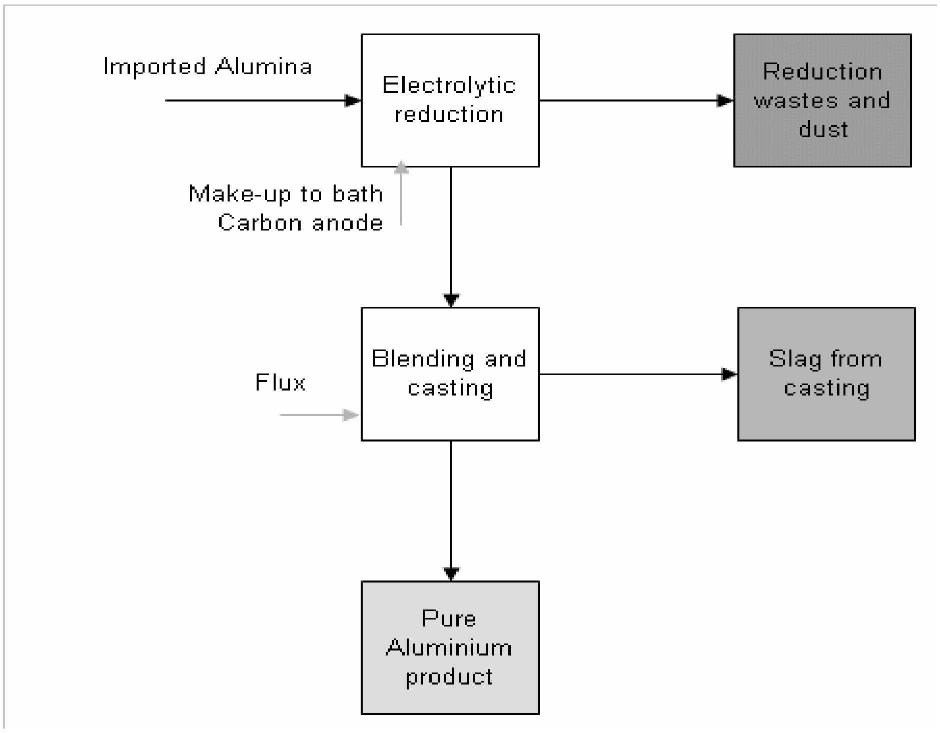
[1] Total wastes from this sector = 11.9 $mt.yr^{-1}$
[2] Total co-disposed liquid volumes = 8500 $Ml.yr^{-1}$

Non-Ferrous Metals Sector

The South African minerals industry also produces a significant amount of non-ferrous metals. These can be sub-divided into the aluminium sub-sector and the base metal sub-sector, the latter incorporating copper, lead and zinc metals. Although essentially a non-ferrous metal, the production of nickel has been included in the platinum industry sector, as the majority of nickel arises as a co-product of this industry.

Aluminium sub-sector:

Generalised process flowsheet for the aluminium sub-sector



Data availability and quality

Data gaps for the aluminium sub-sector

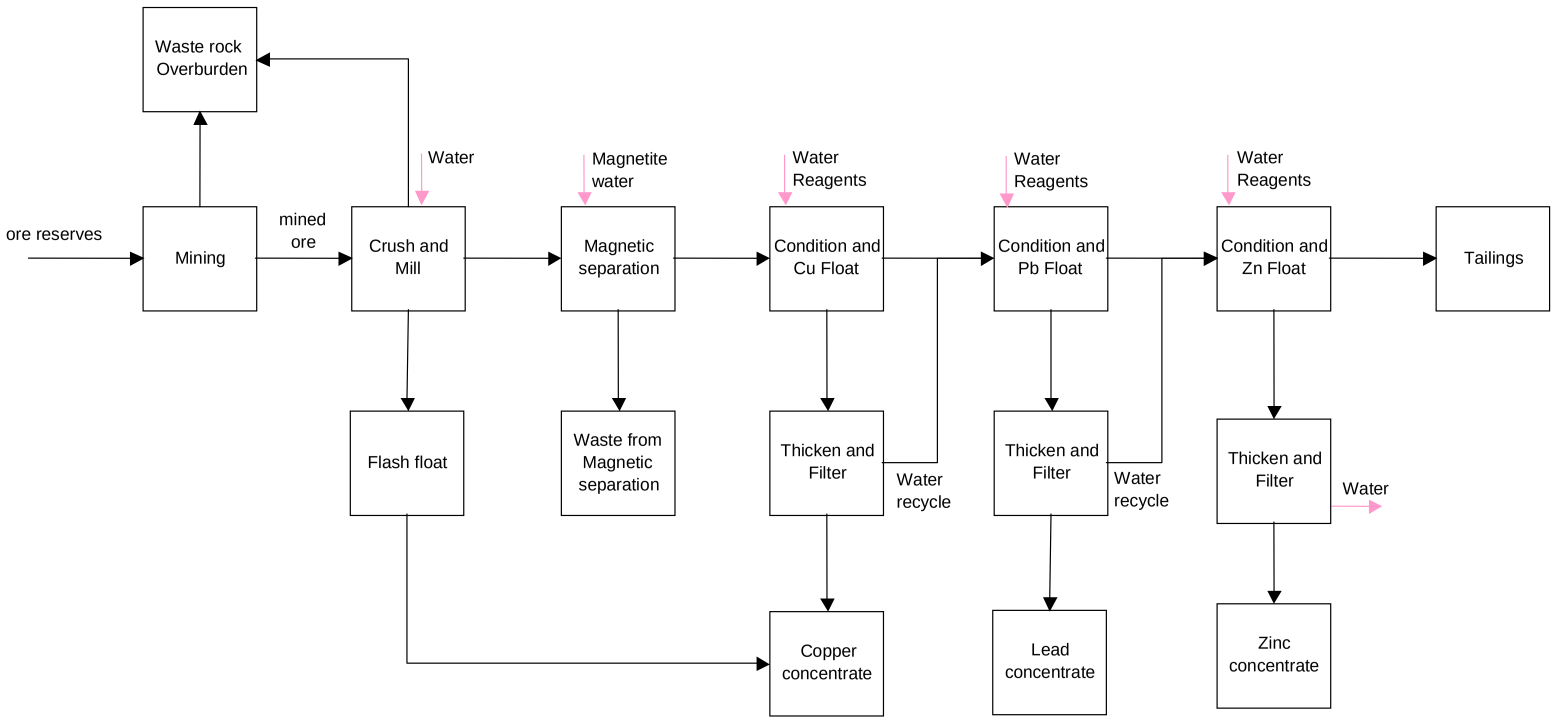
Data requirement	Reduction wastes	Reduction dusts	Blending and casting slag
Waste properties (qualitative)			
Environmental issues			
Process information - Production volumes - S:L ratio - Particle size distribution	✓✓	✓✓	✓✓
Waste management - Deposit area - Technical information - Other information			
Waste characterisation - Components/Mineralogy	✓✓	✓✓	✓✓
Liquid volumes co-disposed - Volume effluent - Quality of effluent			
Leachability studies			

Base-metal sub-sector

Generalised process flowsheets

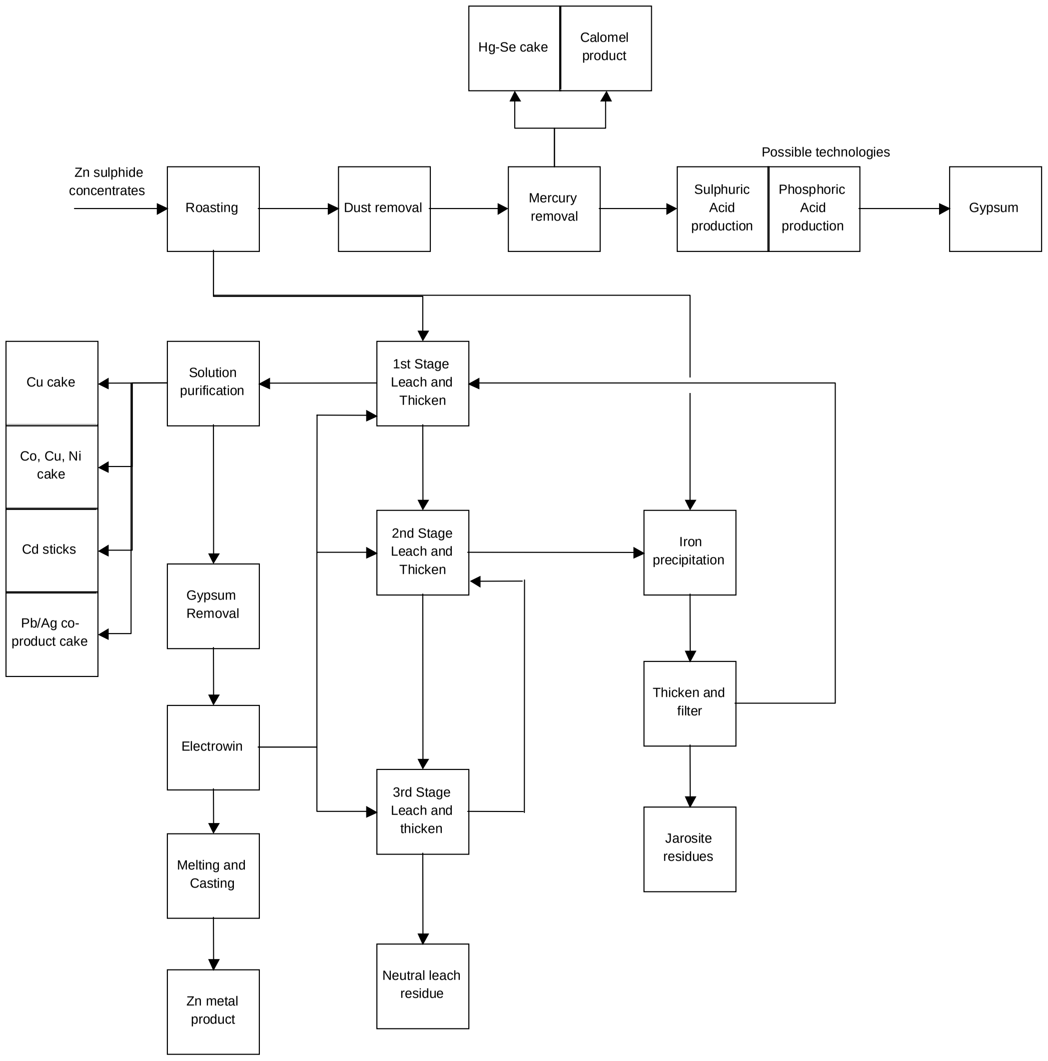
Phosphate is also included in this sub-sector as it is integrated with the production of copper.

Initial concentration flowsheet:



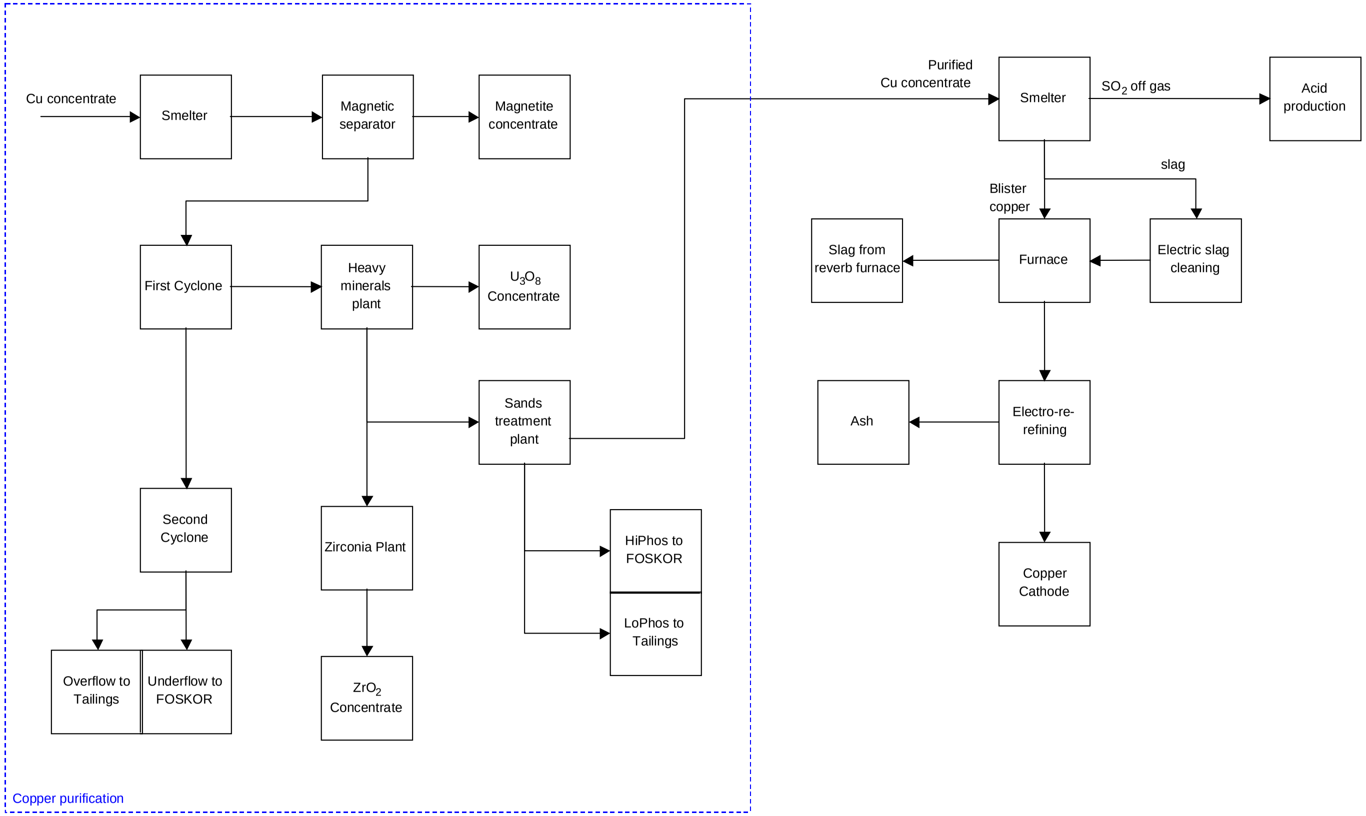
Zinc refining flowsheet:

Zinc metal is produced using a roast-leach-electrowin process. Wastes produced from this process include an Hg/Se cake from mercury removal, jarosite leach residues, neutral leach residues, and a Pb/Ag co-product cake from solution purification.



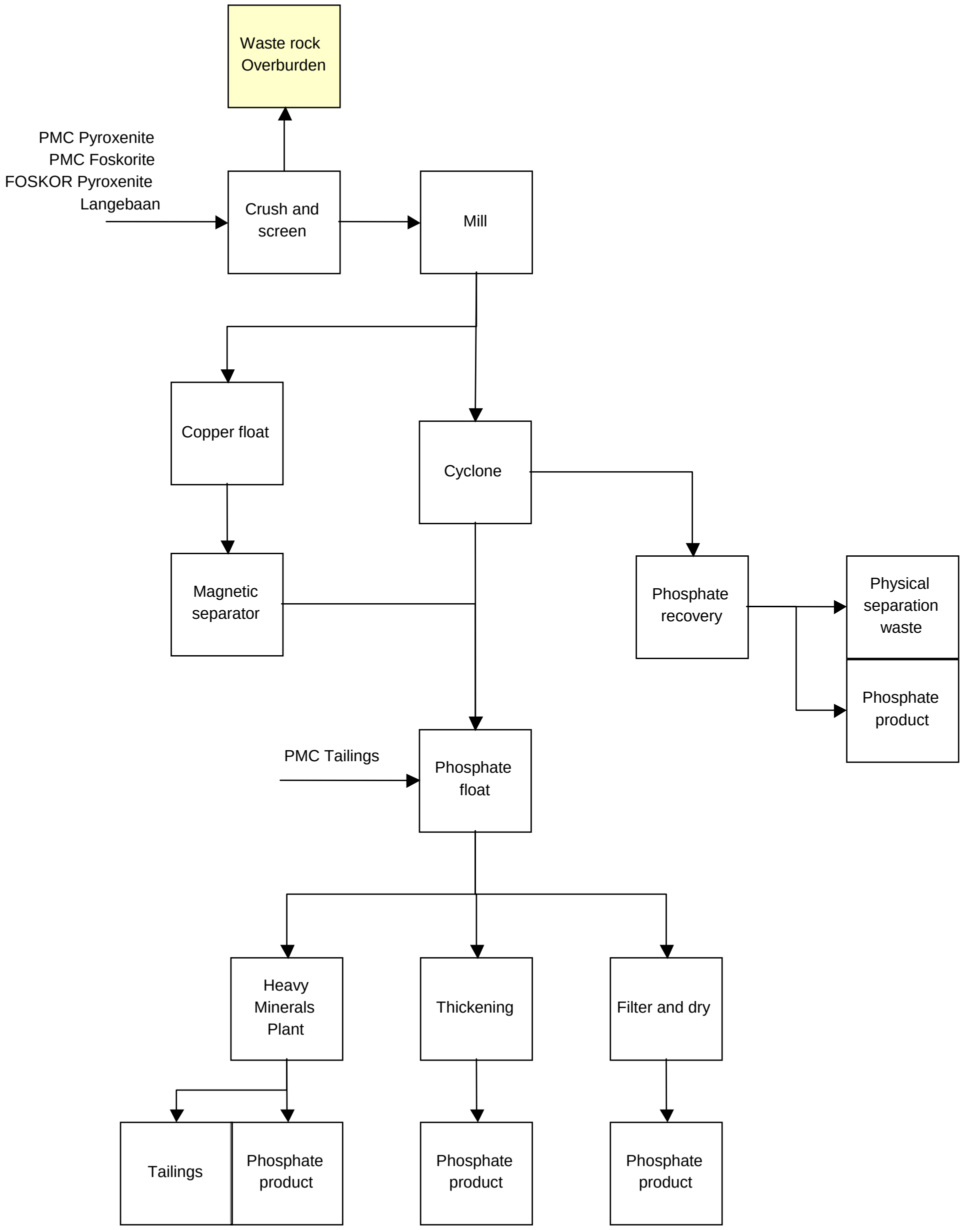
Copper purification and refining flowsheet:

Solids waste generated in the course of this process include tailings from copper purification, furnace slag and residues from electro-re-refining.



Phosphate processing flowsheet:

Although not a metal, the production of phosphate is closely linked to the purification of copper and so is included in the mineral waste inventory. Solids waste streams arise from the physical separation units and the heavy minerals plant.



Data availability and quality

The mineral waste inventory for this sub-sector can be considered to be adequate. For most waste streams the production rate, composition and associated liquid volumes are present. Waste management data and other “difficult to source” information is still lacking.

Data gaps: wastes from initial concentration of Cu/Zn/Pb ores

Data requirement	Waste rock	Tailings from concentration	Magnetic separation waste
Waste properties (qualitative)			
Environmental issues	✓	✓	✓
Process information			
- Production volumes	✓✓	✓✓	✓✓
- S:L ratio	✓✓	✓✓	✓✓
- Particle size distribution			
Waste management			
- Deposit area			
- Technical information			
- Other information			
Waste characterisation			
- Components/Mineralogy	✓✓	✓✓	✓✓
Liquid volumes co-disposed			
- Volume effluent	✓✓	✓✓	✓✓
- Quality of effluent			
Leachability studies			

Data gaps: wastes from production of zinc

Data requirement	Hg-Se cake (mercury removal)	Jarosite residue	Pb-Ag rich residue	Neutral leach residue
Waste properties (qualitative)	✓✓			
Environmental issues	✓✓✓	✓✓	✓	✓
Process information				
- Production volumes	✓✓	✓✓	✓✓	✓✓
- S:L ratio	✓✓	✓✓	✓✓	✓✓
- Particle size distribution				
Waste management				
- Deposit area				
- Technical information				
- Other information	✓✓			
Waste characterisation				
- Components/Mineralogy	✓✓	✓✓	✓✓	✓✓
Liquid volumes co-disposed				
- Volume effluent	✓✓	✓✓	✓✓	✓✓
- Quality of effluent				
Leachability studies				

Data gaps: wastes from production of copper

Data requirement	Tailings from Cu purification	Slag from reverb furnace	Ash from electro re-refining
Waste properties (qualitative)			
Environmental issues	✓	✓	✓
Process information			
- Production volumes	✓✓	✓✓	✓✓
- S:L ratio	✓✓		
- Particle size distribution			
Waste management			
- Deposit area			
- Technical information			
- Other information			
Waste characterisation			
- Components/Mineralogy	✓✓	✓✓	✓✓
Liquid volumes co-disposed			
- Volume effluent	✓✓		
- Quality of effluent	✓		
Leachability studies			

Data gaps: wastes from production of phosphate

Data requirement	Waste rock overburden	Physical separation waste	Tailings from heavy mineral plant
Waste properties (qualitative)			
Environmental issues	✓	✓	✓
Process information			
- Production volumes	✓✓	✓✓	✓✓
- S:L ratio	✓✓	✓✓	✓✓
- Particle size distribution			
Waste management			
- Deposit area			
- Technical information			
- Other information			
Waste characterisation			
- Components/Mineralogy	✓	✓	✓
Liquid volumes co-disposed			
- Volume effluent	✓✓	✓✓	✓✓
- Quality of effluent			
Leachability studies			

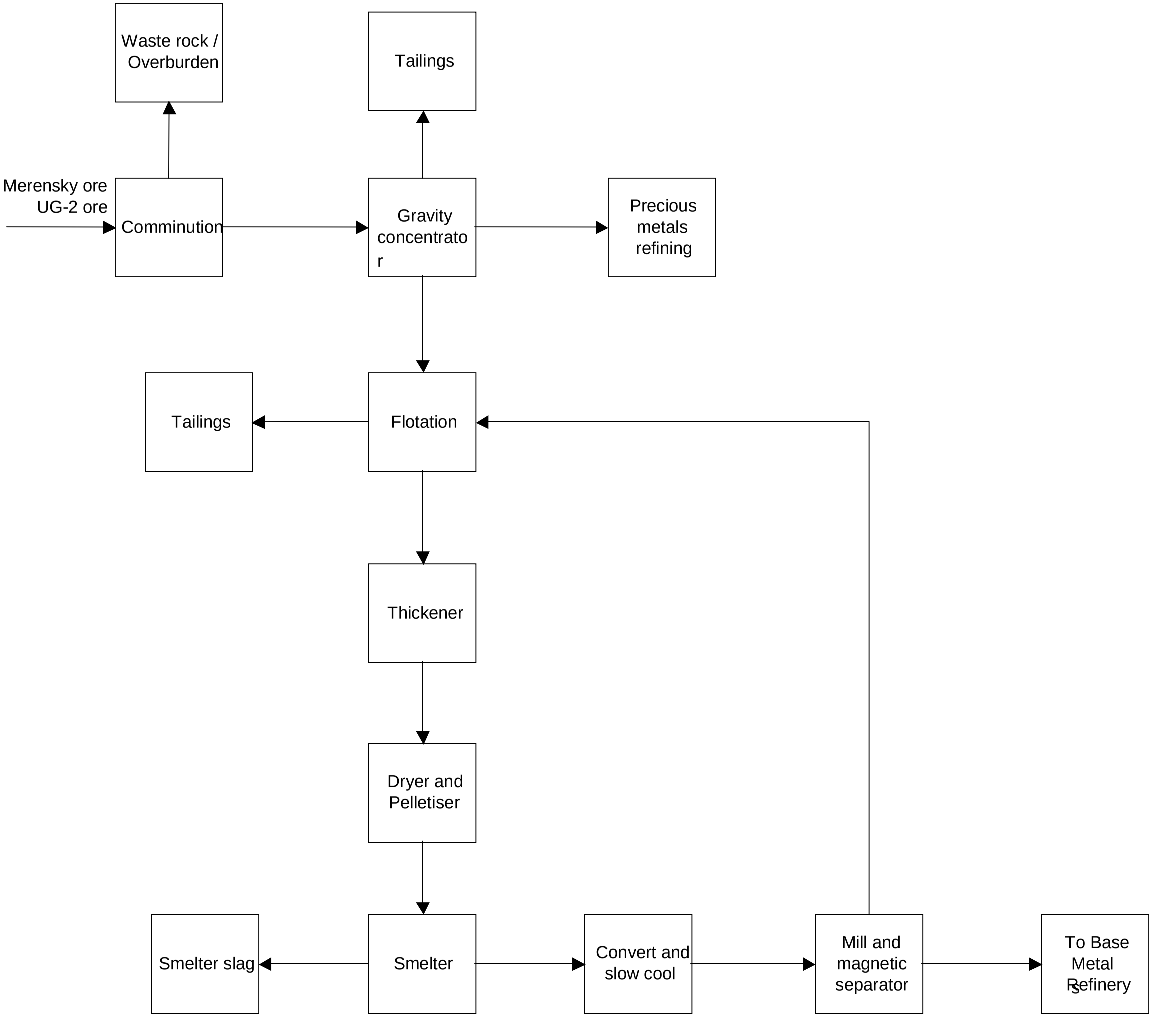
Platinum Group Metals Sector

Generalised process flowsheet for the platinum group metal sector

The six elements concentrated by the platinum group metals (PGM) sector are platinum, palladium, rhodium, ruthenium, iridium and osmium. A number of base metals, including cobalt, copper and nickel, are produced in significant quantities as by products. The platinum group metals sector flowsheet may be subdivided into three activities: initial beneficiation of ores, base metals refining and precious metals refining. Only the former two activities are considered here, as information pertaining to the precious metal refining processes is mostly confidential and difficult to obtain.

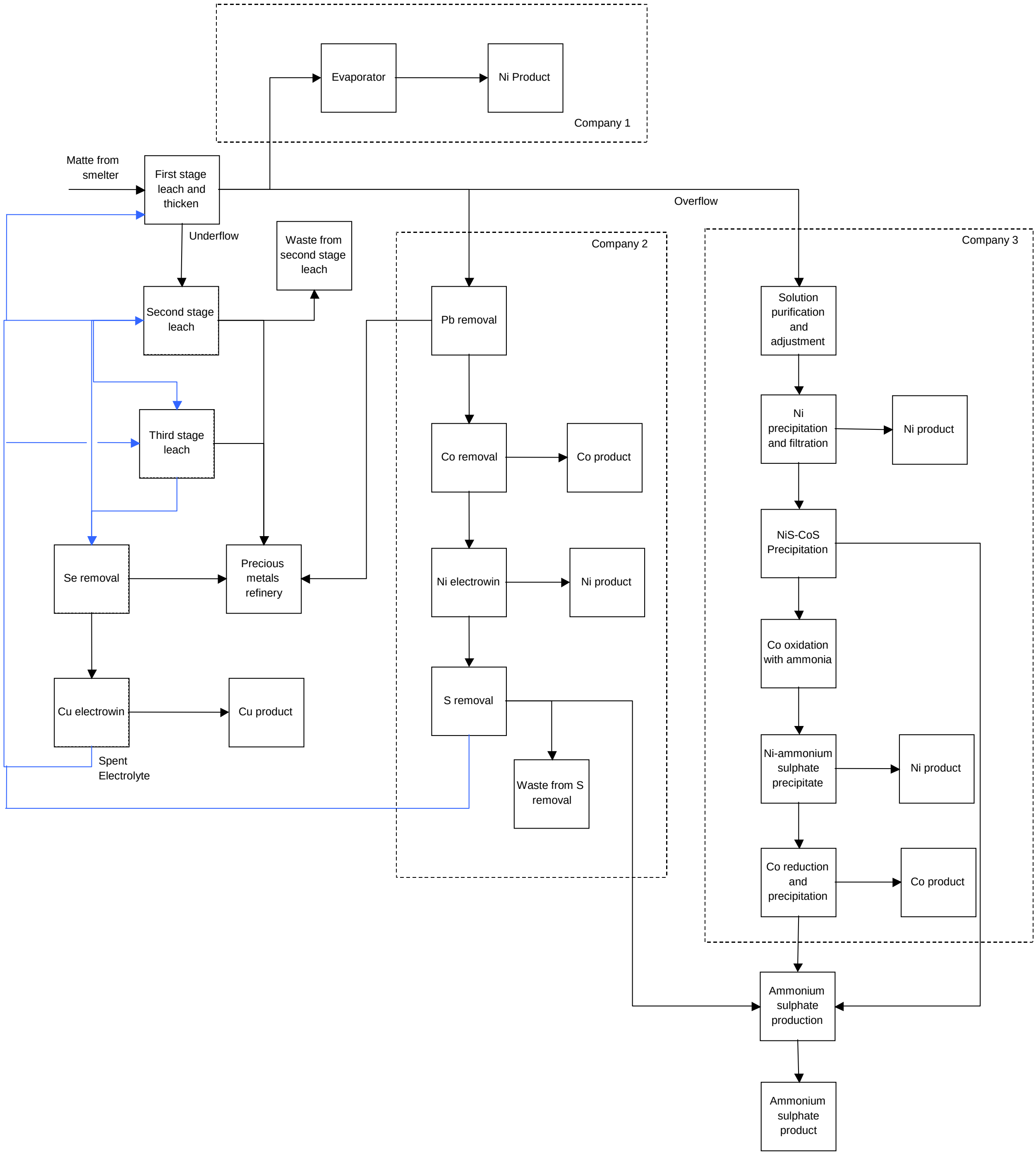
Initial beneficiation of PGM ores flowsheet

The solid wastes arising from this activity include waste rock and overburden from mining, tailings from gravity concentration and flotation, and smelter slag. The UG-2 and Merensky ores differ with respect to the presence of iron and chrome as co-deposited metals (Stewart, 1999).



Generalised flowsheet for base metals refining as part of the platinum group metals industry sector

The flowsheet below includes three different base metal refining operations. Common to all three operations are the three leach stages and the production of copper. The subsequent processes employed for the production of nickel and, optionally, cobalt differ. Only two solid waste streams were identified from this flowsheet: waste arising from the second stage leach and waste arising from sulphur removal (Company 2).



Data availability and quality

Data gaps: initial beneficiation wastes from production of PGMs

Data requirement	Waste rock overburden	Tailings from gravity conc.	Flotation tailings (Merensky)	Flotation tailings (UG-2)	Smelter slag (Merensky)	Smelter slag (UG-2)
Waste properties (qualitative)						
Environmental issues	✓	✓	✓	✓	✓	✓
Process information - Production volumes - S:L ratio - Particle size distribution	✓✓	✓✓ ✓✓	✓✓ ✓✓	✓✓ ✓✓	✓✓ ✓✓	✓✓ ✓✓
Waste management - Deposit area - Technical information - Other information						
Waste characterisation - Components/Mineralogy	✓	✓✓	✓✓	✓✓	✓✓	✓✓
Liquid volumes co-disposed - Volume effluent - Quality of effluent		✓✓	✓✓	✓✓	✓✓	✓✓
Leachability studies						

Data gaps: base metals refining wastes from production of PGMs

Data requirement	Waste from 2nd stage leach	Waste from sulphur removal
Waste properties (qualitative)		
Environmental issues	✓	✓
Process information - Production volumes - S:L ratio - Particle size distribution	✓✓ ✓✓	✓✓ ✓✓
Waste management - Deposit area - Technical information - Other information		
Waste characterisation - Components/Mineralogy	✓✓	✓✓
Liquid volumes co-disposed - Volume effluent - Quality of effluent	✓✓	✓✓
Leachability studies		

APPENDIX B

A GENERALISED METHODOLOGY FOR PREDICTING KEY CONSTITUENTS OF POTENTIAL ENVIRONMENTAL SIGNIFICANCE

On the basis of the qualitative understanding developed in Section 2.2 of this report, the criteria considered to be of key significance in terms of evaluating and prioritising the hazard potential of typical solid mineral waste constituents can be broadly categorised as effect criteria (encompassing biological relevance in terms of toxicity and essentiality, as well as aesthetic and physical properties) and extent of enrichment relative to natural abundance or background levels. These criteria can be quantitatively expressed in terms of effect and enrichment factors, as presented by Equations II.1 and II.2 respectively.

Effect factor = solid concentration/environmentally acceptable concentration	Equation II.1

Enrichment factor = solid concentration/typical background concentration	Equation II.2

Equations II.1 and II.2 can subsequently be combined to provide a quantitative estimate of the hazard potential of the various waste constituents, on the basis of their potential toxicity and human consumption effects as well as their relative abundance, as illustrated by Equation II.3a-b.

Hazard potential factor = (*m.* effect factor).(*n.* enrichment factor)	Equation II.3a
Hazard potential factor = (*m.n*)(solid concentration)^2 /((*m*.environmentally acceptable concentration).(*n*.typical natural concentration))	Equation II.3b
Where *m* and *n* are weighting factors indicating the relative importance of the effect and enrichment factors	

In order to pose an environmental risk, however, waste constituents need to have both an inherent capacity to cause harm or damage *and* be available for release to the surrounding environment. A measure of the *risk* potential thus needs to be based on the hazard potential of that fraction of the waste constituent which is available for release to the environment, rather than on total concentration in the solid waste. Substituting *available* concentration for *total* solid concentration in Equation II.3b provides a quantitative estimate of the risk potential associated with the various waste constituents on the basis of both the hazardous properties and chemical mobility, as illustrated by Equation II.4.

Risk potential factor = (*m.n*)(available solid concentration)^2 /((*m*.environmentally acceptable concentration).(*n*.typical natural concentration))	Equation II.4

The so-called available solid concentrations of the various constituents can, in turn, be derived from the predicted availability potential factors and total constituent concentration levels, as defined by Equation II.5a-b.

Availability potential factor = predicted extent of mobilisation (mass %)/100	Equation II.5a
Available concentration = (availability potential factor).(total solid concentration)	Equation II.5b

In accordance with the chemical behaviour model developed by Broadhurst (2006), the fraction of a solid waste constituent which is mobilised (i.e. rendered available for release to the environment) under disposal conditions can be predicted in a step-wise manner as follows:

1. ***Predict the extent of weathering and/or alteration of primary phases***: The rate and extent to which elements are mobilised through primary weathering and alteration reactions can be predicted on the basis of the forms (or phases) in which they occur within the solid waste, and the time-related reactivity of such phases as a function of redox potential, oxygen concentrations, microbial activity and pH as the main influencing parameters. As discussed in Section 2.2, the rates at which the primary phases are weathered or altered can vary quite considerably, with a number of the primary phases typically occurring in solid wastes from the primary mineral-based resource industries being governed by slow, kinetically-controlled reaction mechanisms. Nevertheless, in many cases the net availability of elements associated with such phases over the life time of the deposit can still be predicted on the basis of thermodynamic considerations. This is because solid waste impacts, and thus the time frames of concern, are generally extremely protracted, frequently extending over hundreds or even thousands of years.
2. ***Predict the extent of secondary attenuation***: Subsequent attenuation of elements mobilised through the weathering and alteration of primary phases can be predicted on the basis of the solubility of their stable forms and/or extent of adsorption onto the surfaces of solid substrates as a function of their activities; the major pore water or leachate chemistry (major soluble ion concentrations, pH and redox potential); as well as the nature and concentration of the major secondary precipitates.
3. ***Predict the overall extent of mobilisation***: Combining 1 and 2 allows for the derivation of the availability potential factor i.e. the net mass fraction of element in the solids predicted to be available for release to the environment over the expected deposit life time (see Equation II.6).

Availability Potential Factor = Reactivity potential factor x (1-attenuation potential factor)	Equation II.6
Reactivity potential factor: The mass fraction of elements in the solids predicted to be mobilised through primary weathering and alteration reactions of the solid phases. Attenuation potential factor: The mass fraction of mobilised elements attenuated through secondary precipitation and adsorption reactions.	

Both the environmentally acceptable risk and typical natural concentration levels, and hence the effect, enrichment and hazard potential factors, of the solid waste constituents will be highly site-specific. Nevertheless, standards such as water quality criteria provide a convenient surrogate measure of acceptable risk concentrations and, if substituted into Equation II.1, can be used to calculate generic effect factors for solid waste constituents. Similarly, generic enrichment factors can be calculated by substituting average crustal abundance values for the solid waste constituents into Equation II.2. On this basis, it is possible to derive generic hard potential factors for solid waste constituents as a function of concentration.

In contrast to hazard potential the mobility of solid waste constituents is influenced by a large number of variables, and it is thus almost impossible to group and rank elements according to their generic mobilities without consideration of the chemical and mineralogical compositions of the solid wastes as a function of ore type and generating processes. Nevertheless, a number of tools exist for predicting the potential chemical mobilities of element constituents within specific solid mineral wastes over the expected deposit life-time on the basis of available empirical data and/or fundamental thermodynamic principles. The most important of these include empirical sequential chemical extraction and standard laboratory leach tests, predictive thermodynamic models, as well as consideration of the periodic properties and trends (periodicity) of the elements.

APPENDIX C

GENERIC LEACHATE GENERATION MODEL STRUCTURE

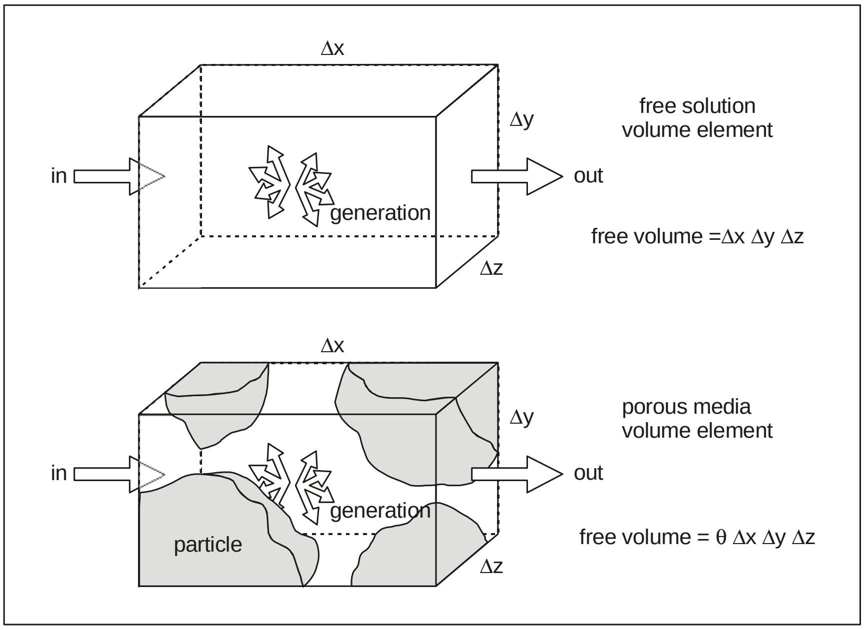
Contaminant transport through porous media

Contaminant transport in the aqueous phase is described for a dissolved species i by the continuity equation for mass transport:

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot N_i + Q_i \,,$$

where N_i is the molar flux of species i, Q_i is a source or sink term corresponding to either the generation or consumption of species i and C_i is the dissolved concentration of i.

In a control volume $\Delta x \Delta y \Delta z$, the concentration of species i within this volume element changes with time according to the mass balance indicated above (i.e. accumulation within the control volume is equal to transport into the control volume less transport out plus generation less consumption). This mass balance is also valid for aqueous transport through porous media (i.e. a waste deposit). However, for porous media only part of the volume element is filled with fluid with the rest of the volume occupied by solid as indicated in the figure below.



Representation of volume elements in free solution and porous media (adapted from Petersen, 1998)

For flow through porous media, the continuity equation must be modified so that all terms are expressed in terms of total volume. As the concentration in the accumulation term is only per unit fluid volume, it must be corrected. The continuity equation now becomes:

$$\theta \frac{\partial C_i}{\partial t} = -\nabla \cdot N_i + Q_i \,.$$

The fraction of space available for fluid relative to the total volume of the bed is the porosity of the bed and is defined below.

$$\theta = \frac{V_{pores}}{V_{total}}.$$

The flux of species i through the bulk phase, N_i, is as a result of three different effects:

- Convection: i moves through the bulk phase under the movement of the entire bulk fluid
- Molecular diffusion: transport of species i is driven by a concentration gradient
- Mechanical dispersion: involves mixing of species. On a macroscopic level mixing is a diffusion-like process, whereas on a macro scale it is influenced by bulk fluid movement (Cussler, 1997)

Therefore the overall molar flux of species i through the bulk phase will be comprised of three components:

$$N_i = N_i^{conv} + N_i^{diff} + N_i^{disp}.$$

Convective mass transport refers to the transport of dissolved species i under the movement of the bulk fluid. This movement is due to the superficial velocity, u, of water through the bed which is defined as the seepage velocity (or Darcy velocity), q, over the bed porosity, θ, such that

$$u = \frac{q}{\theta}.$$

The convective flux in the bulk phase may be expressed as:

$$N_i^{conv} = qC_i.$$

Here the units of flux are [mol.L^{-2}_{total}.T^{-1}] to remain consistent with the chosen units of the continuity equation.

Diffusive flux is a result of the migration of dissolved species from regions of higher concentration to those of lower concentration. Fick's Law is used to describe molecular diffusion for unrestricted flow through a continuous fluid:

$$N_i^{diff} = -D_i \frac{\partial C_i}{\partial z},$$

where, D_i is the molecular or free solution diffusivity which is a dependent on the properties of the solvent, the solute and the presence of other interacting species.

In a porous media, there exist complicated pore structures, and an effective diffusivity is defined by the equation:

$$N_i^{diff} = -D_e \frac{\partial C_i}{\partial z}.$$

This diffusive flux is still per unit area of porous media.

The effective diffusivity is related to the fluid molecular diffusivity by the ratio of the area normal to the direction of the flux available for the molecules to diffuse to total area. For a random pore structure this is equivalent to the void fraction (Froment & Bischoff, 1979). The effective diffusivity also accounts for the fact that the diffusion path length in a porous medium is greater due to the tortuous nature of the pores and that the pores are of varying cross sectional areas. Therefore:

$$D_e = \frac{D_i \theta \sigma}{\tau'} = \frac{D_i \theta}{\tau},$$

where D_e is the effective diffusivity, D_i is the molecular or free solution diffusivity, θ is the bulk porosity, σ is the constriction factor which accounts for the variation in the cross-sectional area that is normal to diffusion and is a function of the ratio of maximum to minimum pore areas. The tortuosity, τ', is defined as the actual distance a molecule travels between two points divided by the shortest distance between those two points. It is not uncommon for the tortuosity and the constriction factor to be lumped together into a tortuosity factor, $\tau = \tau'/\sigma$ (Fogler, 1992).

Mechanical dispersion is the axial spreading of species either longitudinally and, to a lesser extent, laterally to the direction of bulk flow (Fogler, 1992). There are three main contributors to mechanical dispersion: individual pore velocity profiles, differing flow velocities in pores of different diameter, mixing effects related to tortuosity, branching and connection of pores (Freeze & Cherry, 1979).

Mechanical dispersion is analogous to a Fickian diffusion process and is described similarly.

$$N_i^{disp} = -D_m \nabla C_i ,$$

where D_m is the dispersion tensor which is directly related to the seepage velocity, q, by:

$$D_m = \alpha_L q ,$$

where α_L is the dynamic dispersivity with units of length.

Diffusion and dispersion effects can be lumped together as Fick's Law describes them both. The combined diffusion/dispersion constant is referred to as the coefficient of hydrodynamic dispersion, D_L (Bear, 1972).

$$\theta D_L = D_m + D_e = \alpha_L q + \frac{\theta}{\tau} D_i$$

The continuity equation now becomes:

$$\theta \frac{\partial C_i}{\partial t} = -\nabla \cdot \left(qC_i\right) + \nabla \cdot \left(\theta \mathbf{D}_L \cdot \nabla C_i\right) + Q_i ,$$

or in the vertical z dimension:

$$\theta \frac{\partial C_i}{\partial t} = -q \frac{\partial C_i}{\partial z} + \theta D_L \frac{\partial^2 C_i}{\partial z^2} + Q_i .$$

These last two essentially equivalent equations describe the behaviour of a dissolved species as it is transported through a porous media together with a bulk fluid. This equation forms the basis of the conceptual model to describe contaminant transport through the waste deposit.

As the bulk flow has been divided into a dynamic liquid phase and a static liquid phase, two equations are required to describe the movement of species within the bulk fluid. For the dynamic liquid phase:

$$\theta_d \frac{\partial C_d}{\partial t} = D_L \theta_d \frac{\partial^2 C_d}{\partial z^2} - q \frac{\partial C_d}{\partial z} + Q_d .$$

And in the static liquid phase:

$$\theta_{st} \frac{\partial C_{st}}{\partial t} = Q_{st} ,$$

where, C_d and C_{st} are the concentrations of aqueous species in the dynamic liquid and static liquid phases respectively. As the static liquid is not moving, advection and bulk diffusion and dispersion terms are not applicable.

The pore space, θ_b, is partly filled with liquid and the remainder with gas. These are defined as θ_L, liquid-filled pore space and θ_G, gas-filled pore space. The pore space filled with liquid may be further divided into static and dynamic portions – these being θ_{st} and θ_d respectively. More explicitly:

$$\theta_b = \theta_L + \theta_G ;$$

$$\theta_L = \theta_d + \theta_{st} .$$

The fraction of the particle surface which is wetted, denoted by f, may also be divided into the fraction of wetted surface area in contact with static liquid, f_{st}, and the fraction of wetted surface area in contact with dynamic liquid, f_d:

$$f = f_d + f_{st} .$$

Correlations are available to calculate the total wetted surface area or wetting efficiency (Al-Dahhan & Dudukovic, 1995) and the wetted fractions may be approximated using the following relationships developed by Rajashekharam et al. (1998):

$$\frac{f_d}{f} = \frac{\theta_d}{\theta_L} ;$$

$$\frac{f_{st}}{f} = \frac{\theta_{st}}{\theta_L} .$$

As the dynamic liquid is in contact with both the static liquid and the particle surface, the term Q_d needs to account for transport to these phases as well as possible surface and/or liquid phase reaction. The continuity equation for the dynamic liquid phase then becomes:

$$\theta_d \frac{\partial C_d}{\partial t} = D_L \theta_d \frac{\partial^2 C_d}{\partial z^2} - q \frac{\partial C_d}{\partial z} - k_a \theta_d (C_d - C_{st}) - D_{eff} a_s f_d \left. \frac{\partial C_p}{\partial r} \right|_{r=R} + \sum R_d .$$

Similarly, the static liquid equation becomes:

$$\theta_{st} \frac{\partial C_{st}}{\partial t} = -k_a \theta_{st} (C_{st} - C_d) - D_{eff} a_s f_{st} \left. \frac{\partial C_p}{\partial r} \right|_{r=R} + \sum R_{st} .$$

In the above equations, k_a represents the mass transfer coefficient between static and dynamic liquid hold-ups [T^{-1}], D_{eff} is the effective diffusivity through the particle pores [$L^2.T^{-1}$], a_s is the specific area which is calculated as the surface area of particles divided by the bed volume [$L^2.L^{-3}$] and C_p is the concentration of species within the particle pores. R_d and R_{st} represent possible surface reactions and liquid phase reactions within the dynamic and static regions.

The incorporation of a static and dynamic liquid flow structure increases the complexity of the bulk flow model with respect to hydrodynamic behaviour. Inclusion of a static region allows the effects of back-mixing to be modelled. Back-mixing gives rise to the extended tails observed in residence time distribution (RTD) studies. However, while this flow structure does not explicitly account for preferential flow paths, the fact that there are two fluid phases with different velocities (0 and q) and mass transfer between these phases, this phenomenon is perhaps incorporated.

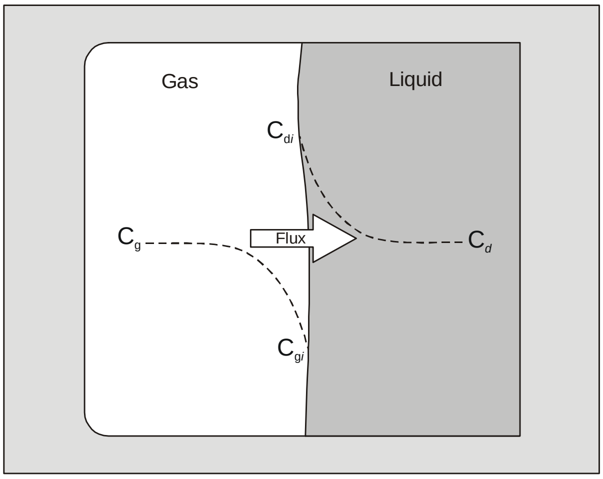
The transport of gaseous species present in air, such as O_2 and CO_2, which is considered a key rate limiting process in acid mine drainage, warrants inclusion in the generic conceptual model. While some researchers have considered specifically oxygen transport in attempts to model acid mine drainage and heap leaching, these approaches typically only consider oxygen transport in the gas phase and a sink term for oxygen consumption. Not many researchers have considered oxygen transport into the bulk fluid and transport and reaction within this phase or indeed the particle pores.

It was decided in this work to treat gaseous reactants as all other reactants and aqueous species. Thus, transport of gaseous components both within the air-filled pore space and from the air-filled pore space into other phases is considered in the conceptual model. The assumption is made that air in the air-filled pore space is immobile and gaseous components are transported by diffusion only. The resulting continuity equation for gaseous components is:

$$\theta_G \frac{\partial C_g}{\partial t} = \theta_G D_A \frac{\partial^2 C_g}{\partial z^2} - Q_g \, .$$

As mentioned previously, some researches assume that oxygen diffusion is rate limiting. As a result, Q_g represents the rate of oxygen consumption occurring at a reaction interface. This assumption is only valid for pyritic wastes in waste deposits of sufficient depth. As it is an objective of this work to develop a generic model, it must be applicable not only to pyritic wastes but also wastes where oxygen transport is not rate limiting or is unimportant. It must also be noted that the above equation is not limited to oxygen and transport of other gaseous components must be able to be described by this equation, for example CO_2. In these cases Q_g represents transport to the dynamic liquid phase. Direct gaseous transport to the static liquid phase is not included as it is an assumption of the flow structure (represented by Figure 2.11 in Section 2.4.1 of the report) the static liquid phase is bounded by dynamic liquid and the particle surface (i.e. no static liquid is open to air-filled pore space).

To determine the mass transfer of gaseous species from the air-filled pore space to the dynamic liquid phase, the two-resistance concept is employed. The driving force for mass transfer is the concentration gradients in the direction of mass transfer, which exist within each phase, and is depicted in the diagram below.



Mass transfer across a gas-liquid interface – the two-resistance concept (adapted from Cussler, 1997)

In this figure, C_g and C_d represent the bulk concentrations in the gas and dynamic liquid phases respectively. These concentrations are clearly not at equilibrium, as diffusion would not occur if they were. The concentration of gaseous species in the bulk gas, C_g, drops to C_{gi} at the interface between the gas and the liquid, while the concentration in the dynamic liquid drops from C_{di} at the interface to C_d in the bulk liquid. The two-resistance theory assumes that the only resistances to diffusion are in the fluids and that there is no resistance to mass transfer across the interface. As a result, C_{gi} and C_{di} are at equilibrium. In the figure, C_{gi} and C_{di} are not shown to be equal; this is because concentrations in a gas phase are usually expressed in mole fractions while those in a liquid phase are expressed in concentrations. The flux for both phases is given by:

$$N_g = k_G (C_g - C_{gi});$$

$$N_d = k_L (C_{di} - C_d),$$

where k_L and k_G represent mass transfer coefficients [$L.T^{-1}$].

As the concentrations at the interface cannot be measured, the flux needs to be stated in terms of the bulk concentrations. The concentrations at the interface are, however, at equilibrium and may be related via Henry's law:

$C_{gi} = H_c C_{di}$,

where H_c is the Henry's law constant.

At steady state the fluxes N_g and N_d are equal. Equating the two flux equations and replacing C_{gi} with $H_c \times C_{di}$, C_{di} may be solved for:

$$C_{di} = \frac{k_G C_g + k_L C_d}{k_L + k_G H_c} .$$

Substituting back, the flux in terms of the bulk concentrations is found to be:

$$N = \frac{C_g - H_c C_d}{\frac{1}{k_G} + \frac{H}{k_L}} .$$

This term may be substituted into the equation describing transport in the air-filled pore spaces after correcting with a suitable specific area term, a_g, the surface area of dynamic liquid divided by the volume of gas. The gas-phase continuity equation then becomes:

$$\theta_G \frac{\partial C_g}{\partial t} = \theta_G D_A \frac{\partial^2 C_g}{\partial z^2} - a_g \left(\frac{C_g - H_c C_d}{\frac{1}{k_G} + \frac{H}{k_L}} \right) .$$

The final term in this equation must be added to the dynamic liquid equation of the species which diffuses into the liquid phase.

The three continuity equations derived above along with appropriate boundary and initial conditions effectively describe the transport and reaction of contaminants in the gaseous, dynamic liquid and static liquid phases and form the basis of the generic conceptual model.

Contaminant release and attenuation

The source or sink term, Q_i, found in the continuity equations derived above accounts for the generation or consumption of species i. There are a number of mechanisms by which contaminants or chemical species may be removed from or introduced into the bulk fluid. These include:

- Chemical reaction with other dissolved or solid species
- Dissolution or precipitation of a solid species
- Sorption or desorption from a solid surface

As all of these mechanisms might play a role the source or sink term, Q_i, represents the sum of the rate at which these processes occur.

Many reactions may be described by a kinetic rate function, such as:

$$Q_i = \frac{\partial C_i}{\partial t} = f(k, C_i, \ldots C_n) .$$

In these cases, the rate of reaction of species i is described by some function, f, which involves a kinetic rate constant, k, and the product of the concentration of one or all of the species involved raised to an appropriate power. The exact form of the rate expression and the value of the rate constant are found by appropriate waste characterisation and laboratory experiments.

Processes that may be described by kinetic expressions include leaching, oxidation-reduction reactions and precipitation-dissolution processes.

Reactions that are sufficiently fast so that they can be considered instantaneous may be represented by an equilibrium relationship. As these reactions occur very fast, rate constants are difficult to measure and the reaction is described by an appropriate thermodynamic equilibrium model:

$$K_{eql} = \prod_i a_i^{\alpha_i} ,$$

where, K_{eql} is the thermodynamic equilibrium constant, a_i is the activity of species i and α_i represents the stoichiometric coefficient of species i in the reaction. The equilibrium constant is determined through minimisation of the Gibbs free energy or from experimental values.

The activity of solution species is defined as:

$$a_i = \gamma_i m_i ,$$

where γ_i is the activity coefficient and m_i is the molality of species i.

Speciation reactions are typically described by equilibrium relationships. However, incorporating equilibrium speciation modelling represents a significant modelling challenge, due to the large number of species typically present in leachates from solid wastes. Nevertheless, the equations derived here are the starting point to describe contaminant transport through waste deposits.

Data requirements and sources of information

For the generic model developed above, the parameters that need to be determined are listed in the table overleaf, together with the source of data.

Many of the parameters required for leachate generation modelling can be obtained from literature sources. However, care must be taken to ensure that the literature values are applicable to the waste deposit situation. Reaction rates, for example, determined in high-temperature laboratory experiments are not applicable to the ambient conditions found in waste deposits, unless temperature dependence is stated. Correlations are also available to calculate mass transfer coefficients and diffusivities amongst others. Other data must be collected from the actual waste deposit site. This data includes rainfall rates and likely concentrations, waste deposit height and geometry and other site-specific data.

Leachate generation model parameters

Description	Parameter	Units	Data source
Species parameters			
Number of aqueous components	n_c	-	Consequence of the conceptual model
Molecular diffusivity	D_i	$L^{2}.T^{-1}$	Correlation, Literature values
Particle parameters			
Fraction of internal/particle pore space	θ_p	$L^{3}.L^{-3}$	Experimental
Wetted fraction of particle surface	f	$L.L^{-1}$	Estimated
Dynamic wetted fraction of particle surface	f_d	$L.L^{-1}$	Calculated
Static wetted fraction of particle surface	f_{st}	$L.L^{-1}$	Calculated
Specific area (surface area of particles/bed volume)	a_s	$L^{2}.L^{-3}$	Calculated, estimated
Average particle radius or particle size distribution	R	L	Experimental
Density of particle (bulk density not true density)	ρ_p	$M.L^{3}$	Experimental
Bulk fluid parameters			
Bulk porosity	θ_b	$L^{3}.L^{-3}$	Calculated from experiment
Fraction of pore space filled with dynamic liquid	θ_d	$L^{3}.L^{-3}$	Estimated
Fraction of pore space filled with liquid	θ_L	$L^{3}.L^{-3}$	Calculated from experiment
Fraction of pore space filled with static liquid	θ_{st}	$L^{3}.L^{-3}$	Estimated
Height of deposit	Z	L	Site-specific
Mass transfer coefficient between static and dynamic liquid hold-up	k_a	T^{-1}	Correlation
Darcy velocity	q	$L^{3}.L^{-2}.T^{-1}$	Calculated based on rainfall
Hydrodynamic dispersion coefficient	D_L	$L^{2}.T^{-1}$	Calculated
Dynamic dispersivity	α	L	Literature
Bulk fluid tortuosity factor	τ	-	Literature
Density of liquid	ρ	$M.L^{-3}$	Literature
Viscosity of liquid	μ	$M.L^{-1}.T^{-1}$	Literature
Bulk gaseous parameters			
Number of gaseous species	n_g	-	Consequence of conceptual model
Fraction of pore space filled with gas	θ_G	$L^{3}.L^{-3}$	Calculated
Oxygen diffusion coefficient through waste deposit	D_G	$L^{2}.T^{-1}$	Experimental, literature
Gas phase mass transfer coefficient	k_G	$L.T^{-1}$	Literature
Liquid phase mass transfer coefficient	k_L	$L.T^{-1}$	Literature
Henry's law coefficient	H_c	-	Literature
Surface area of dynamic liquid/Volume of gas	a_G	$L^{2}.L^{-3}$	Calculated
Reaction parameters			
Number of solid reactants	n_s	-	Consequence of conceptual model
Number of reactions	n_r	-	Consequence of conceptual model
Stoichiometric coefficient matrix	s	-	Experimental, literature
Rate constant matrix	k_r	variable	Experimental, literature

APPENDIX D

FATE AND TRANSPORT MODELLING ASSUMPTIONS, CONSEQUENCES AND RESOLUTIONS

Modelling Assumption	Consequence	Resolution
Vadose zone is not modelled effectively. Although MODFLOW and MT3D allow an unsaturated zone above an aquifer to be incorporated, these areas are treated as inactive in terms of flow and solute transport. As a result leachate is applied to the highest active cells and transport through and possible reaction in unsaturated zones are ignored	Pollution plume is *over-estimated* as transport through the unsaturated zone and attenuation within the unsaturated zone is ignored.	Specialised vadose zone model linked to a saturated groundwater flow and mass transport model, however, this would increase model complexity and effort. An alternative solution would be to model a saturated aquifer thus eliminating the need for an unsaturated zone.
Waste deposit area is assumed constant	This would *initially overestimate* the contaminated land area or volume but as time progressed the affected land volume would average out.	A time dependent source term would resolve this. Alternatively the average area may be used, recognising the potential error arising.
Adsorption represented by a retardation factor. The retardation factor is in essence a lumped parameter incorporating a number of effects from a variety of variables, and its development is not thermodynamically rigorous. The mechanisms of sorption as well as the effects of pH, redox conditions, ionic strength, complexation and competitive adsorption are ignored or assumed constant.	If a linear adsorption isotherm is used, an infinite amount of solute may be adsorbed, thereby *underestimating* the affected land volume. Ignoring competitive adsorption effects would also *underestimate* the affected land volume. Disregard of reduced solute concentrations due to pH effects, redox conditions, ionic strength and complexation would *overestimate* the affected land volume.	Alternative approaches for considering adsorption require a large number of parameters and rigorous surface characterisation and are probably not appropriate to use for a generic model. As the retardation factor approach is widely accepted, it should be used here whilst fully recognising its limitations.
Homogeneous subsurface environment	Depending on the heterogeneities the affected land volume could be increased or decreased. The pollution plume would most likely be an irregular shape and the volume more difficult to calculate.	Unless generic heterogeneities can be identified, a homogeneous subsurface environment is the simplest scenario to consider.

Modelling assumption	Consequence	Resolution
In 2D model instantaneous vertical mixing is assumed	If the aquifer is relatively thin, this assumption may be used. However, it is less applicable to thicker aquifers especially considering the fact that vertical hydraulic conductivity is often orders of magnitude less than horizontal hydraulic conductivity. It is difficult to determine whether the affected land volume will be over- or underestimated in this case.	A 2D model may be adequate for determining an affected land volume, if it can be assumed that thinness is a generic aquifer property.
Interactions between species ignored	MT3DMS allows a number of non-interacting species to be modelled simultaneously. Ignoring complexation reactions and inter-species reactions that would decrease free ion concentrations *overestimates* the affected land volume.	Multiple species and their reactions may be included by employing MT3DMS rather than MT3D as the mass transport code and by adding on an associated geochemical model, if complex reactions are to be considered.
Geochemical reactions/speciation reactions ignored	Geochemical reactions would reduce the free ion in solution, thus this assumption *overestimates* the affected land volume.	Incorporating geochemical and speciation reactions requires an add-on geochemical model.
Density effects of high salinity plume ignored	Increased salinity increases the density. Hydraulic head and hydraulic conductivity are both functions of density with hydraulic head having an inverse relationship and hydraulic conductivity a direct relationship. Although it is difficult to determine, ignoring density effects would *underestimate* the affected land volume.	The governing equation to be solved must be written in terms of pressure head and intrinsic permeability. A special numerical model incorporating density effects may be used.
Interactions between metals and salinity are ignored	Again, the limitations imposed by the mass transport model mean that interactions between salts and metals cannot be effectively incorporated. However, if the assumption is made that the pH and redox conditions remain unchanged in the subsurface environment, then the impact of salinity on metals is to increase their mobility. Ignoring interactions would therefore *underestimate* the land volume affected by metals.	Interactions between metals and salts could qualitatively be incorporated into the mass transport model by reducing the retardation factor of the particular metal in the area impacted by salinity. Alternatively the add-on geochemical and speciation reaction package would incorporate these interactions.

APPENDIX E

AVAILABLE DATA PERTAINING TO COPPER SULPHIDE ORE AND SULPHIDE TAILINGS DEPOSITS

E1 Chemical compositions of copper sulphide ore deposits

Element	Porphyry deposits (du Bray, 1996; Bulatovic, 1998)			Skarn deposits (du Bray, 1996)			Unspecified deposits (see references 1-4, 11,12 & 16 in Appendix E.3)	
	min	max	mean	min	max	mean	min	max
Si %	21	35	31	n.d.	n.d.	n.d.	30.4	n.d.
Al %	4	9.5	6.5	n.d.	n.d.	n.d.	n.d.	n.d.
Fe %	0.05	10	3.2	n.d.	n.d.	n.d.	1.5	29.4
K %	0.1	8.7	2.7	n.d.	n.d.	n.d.	n.d.	n.d.
S %	0.4	8	1.9	n.d.	n.d.	n.d.	1.4	n.d.
Mg %	0.02	6.6	3	n.d.	n.d.	n.d.	n.d.	n.d.
Na %	n.d	3.7	0.6	n.d.	n.d.	n.d.	n.d.	n.d.
Ti %	0.1	1	0.4	n.d.	n.d.	n.d.	n.d.	n.d.
Cu %	0.8	2.2	0.33	n.d.	13.5	0.6	0.58	0.86
Ca %	0.06	5	0.32	n.d.	n.d.	n.d.	5.3	n.d.
Ba ppm	50	5000	455	n.d.	2200	645	n.d.	n.d.
Mn ppm	0.1	5000	366	n.d.	4670	848	50	n.d.
Sr ppm	n.d	800	207.5	n.d.	n.d.	n.d.	n.d.	n.d.
Rb ppm	20	500	139	n.d.	n.d.	n.d.	n.d.	n.d.
Zr ppm	n.d	320	118	n.d.	n.d.	n.d.	n.d.	n.d.
Zn ppm	<5	17000	94	4	132700	1669.0	4600	9300
V ppm	0.13	700	74	n.d.	n.d.	n.d.	n.d.	n.d.
Pb ppm	2	10000	42	3	132000	1610	1000	n.d.
B ppm	n.d.	2000	36	n.d.	n.d.	n.d.	n.d.	n.d.
Cr ppm	n.d.	1000	33	n.d.	674	105	n.d.	n.d.
Ni ppm	<5	200	20.7	1.0	152.0	34.0	n.d.	n.d.
Mo ppm	<5	2000	20.0	1.0	275.0	22.0	n.d.	n.d.
Li ppm	n.d.	358	18.4	n.d.	n.d.	n.d.	n.d.	n.d.
Co ppm	n.d.	150	18.0	n.d.	275.0	22.0	n.d.	n.d.
As ppm	n.d.	1200	15.5	n.d.	289.0	69.0	4100.0	4500
W ppm	<3	150	7.4	n.d.	316	41	n.d.	n.d.
Sb ppm	n.d.	1500	4.7	n.d.	580	25.0	1500	13100
Sn ppm	n.d.	70	4.6	n.d.	n.d.	n.d.	1800	n.d.
Se ppm	n.d.	20	4.5	n.d.	420	31	10	80
Ag ppm	n.d.	150	1.2	n.d.	300	14	50	n.d.
Bi ppm	n.d.	500	1.1	n.d.	1505	46	0.2	70
Be ppm	n.d.	2	1.1	n.d.	n.d.	n.d.	n.d.	n.d.
Cd ppm	n.d.	150	0.3	n.d.	n.d.	n.d.	n.d.	n.d.
Te ppm	n.d.	3000	0.3	n.d.	76	6	n.d.	n.d.
Au ppm	n.d.	3.0	0.1	n.d.	176	3	81.0	n.d.
Hg ppm	n.d.	1.1	0.1	n.d.	1.9	0.1	n.d.	n.d.
Tl ppm	n.d.	n.d.	n.d.	n.d.	2.3	0.8	n.d.	n.d.
In ppm	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1	1
Ge ppm	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Re ppm	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	10	2000

Typical mineralogical compositions of copper sulphide deposit classes (after Cox & Singer, 2003; Cox et al. 2003; du Bray, 1996; Seal & Foley, 2002)

Deposit Class	Porphyry	Skarns.	Polymetallic vein and replacement	Sedimentary	Massive volcanogenic	Ultrabasic magmatic	Carbonatite magmatic
Major ore minerals	Bornite, chalcopyrite, magnetite, pyrite molybdenite,	Arsenopyrite, bornite, chalcopyrite, hematite, pyrite, pyrrhotite, sphalerite.	Bornite, chalcopyrite, galena, hematite, pyrite, sphalerite,	Chalcopyrite, chalcocite, pyrite, bornite	Chalcopyrite, pyrite, marcasite, pyrrhotite, sphalerite	Chalcopyrite, cobaltite, pentlandite, pyrrhotite.	Apatite, chalcopyrite magnetite, pyrite, pyrrhotite,
Minor ore minerals	Electrum, galena, sphalerite, tetrahedrite	Bismutite, cobaltite, electrum, enargite, galena, molybdenite, scheelite, stannite, sulfosalts, tetrahedrite group	Acanthite, arsenopyrite, electrum, marcasite, stibnite, sulfosalts, tetrahedrite group, bismutite.	Galena, sphalerite,	Arsenopyrite, galena, stannite, bornite, electrum, tetrahedrite group	Telluride's, arsenides, antimonides, bornite, PGMs	Niccolite, monazite, barite, pyrrhotite, molybdenite, galena, sphalerite, columbite
Supergene ore enrichment	Chalcocite, covellite	Covellite			Covellite, chalcocite, digenite		
Major gangue minerals	Albite, alunite, amphibole, anhydrite, biotite, chlorite, clays, epidote, quartz and tourmaline.	Amphibole, chlorite, epidote, garnet, quartz, vesuvianite, wollasinite	Adularia, alunite, barite, calcite, chalcedony, chlorite, clays, fluorite, kaolinite, muscovite, pyrophyllite, quartz,, rhodochrosite, siderite	Dolomite, limestone, shales and calcsilicates	Albite ,amphibole ,chlorite muscovite quartz, tourmaline		Calcite, dolomite, ankerite, ilmenite, strontianite, fluorite, biotite, pyroxenes, amphiboles, fosterite, haematite, zircon, rutile, brookite, anatase.
Minor gangue minerals	Andalusite, calcite,	Fluorite					
Reported co-elements	Up to 28 elements reported: Ag*, As*, Au*, B, Ba, Bi, Cd, Co, Hg, K, La, Li, Mn, Mo*, Ni, Pb*, Rb, Se*, Sn, Te* , Tl, U, V, W, Zn,	Ag,* As, Au*, B, Ba, Bi, Co, Cr, Hg, Mo, Pb*, Rb, Sb, Se, Sn, Sr, Te, W, Zn*	Ag*, As*, Au*, Ba, Bi, Hg, Mn, Mo, Pb*, Sb, Sn, Zn*	Ag* (max 200ppm), As, Au, B, Ba, Bi, Cd, Co*, (max >1%), Cr, Ge, Hg, Mo, Pb*, Sc, U, V, Zn*,	Al, As, Ag*(max 60ppm), Au (4 ppm), B, Ba, Bi, Co, Cr, Ni, P, Pb, Sb, Se, Sn, W, Zn,	Ni*, Co*, Mg, PGE* Where: Pt/Ni=1/500 and Ni/Co= 0.5-1.5/1	B, Ba, Be, Ca, Li, Mo, Nb*, P, Pb, REE*, Sr, Ta, Th*, Ti, U*, V, W, Zn, Zr*

Where: * represents signature elements, commonly associated with copper ore deposit classes

E2 Mining and concentration input-output stream compositions

Elemental compositions

Element	Run-of-mine ore (kg/t)	Concentrate (kg/t)	Tailings (kg/t)	Waste rock (kg/t)
Major ore components				
Copper	1.8-22(1,11,12,14, 18)	137-471(1, 2,3,4,5,6,11,12, 18)	0.3-20(1,3,7,8,11,12,17)	0.7-3.6(10,13)
Iron	0.5-294(1,12,14)	85-330(1, 2,3,4,5,12)	9-740(1,3,7,8,12,17)	27-68(10,13)
Sulphur	4-80(1,14)	150-370(1,2,3,4,5)	3-109(1, 3,6,7,9)	7-389(9,13)
Minor ore components				
Arsenic	0.02-4.5(1,12,14)	0.15-80(1, 2,3,4,12)	0.03-4.5(1 3,7,12)	n/a
Lead	<0.1-132(1,14)	0.14-6.7(1, 2,3)	0.01-0.9(1, 3,7,17)	n/a
Molybdenum	<0.1-2(14,18)	0-12.7(2,3,18)	0.03-0.5(3,7)	n/a
Zinc	<0.1-133(1,12,14)	0.2-40(1, 2,3,12)	0.02-4.3(1, 3,7,12,17)	0.1-0.8(13)
Trace ore components				
Antimony	0.05-13.1(1, 2,3,4,11,14)	0.02-5(1,2,3,4,12)	0.07-13.1(3,7,12)	n/a
Bismuth	0.0002-1.5(1, 2,3,4,11,14)	<0.03-0.9(2,3)	<0.1(3)	n/a
Boron	0.04-2(14)	<0.002-0.1(2,3)	n/a	n/a
Cadmium	<0.001-0.2(14)	0-0.09(2,3)	<0.1(3)	n/a
Chromium	0.03-1(14)	0.02-0.14(2,3)	0.005-0.3(3,7)	n/a
Cobalt	0.02-0.3(14)	0.02-0.29(2,3)	1.4(3)	n/a
Germanium	n/a	2.9(3)	n/a	n/a
Gold	<0.001-0.18(2,14)	0.0002-0.07(1, 2,3,4,11)	0.0001-0.0002 (11)	n/a
Indium	0.0005-0.001(11)	0.03-0.26(3,12)	0-0.0005(3,12)	n/a
Manganese	<0.05-5(12,14)	0.05-0.17(2,3)	0.05-1(3,7)	<3.1(13)
Mercury	<0.001-0.002(14)	<0.0002-0.24(2,3,12)	0.008-0.014(3,12)	n/a
Nickel	<0.0001-0.2(14,15)	0.1(2)	0.2(3)	n/a
Palladium	n/a	0.00003-0.00005(15)	n/a	n/a
Platinum	n/a	n/a	n/a	n/a
Phosphorous	n/a	0.13-1.01(2,3)	4.7(3)	n/a
Rhenium	0.01-2(16)	n/a	n/a	n/a
Selenium	0.005-0.4(14,16)	1.96(3)	<0.1(3)	n/a
Tellurium	<0.005-3(14)	<0.005-0.02(2,3)	n/a	n/a
Thallium	<0.001-0.002(14)	0.00(3)	n/a	n/a
Silver	0.001-0.3(12,14)	0.02-1.3(1, 2,3,4,12)	0.004-0.01(3,12)	n/a
Tin	0.005-1.8(12,14)	<0.003-4.6(2,3,12)	<0.1-0.2(3,12)	n/a
Titanium	1-10(14)	0.12-5(2,3)	0.5-3.6(3,7)	<4.2(13)
Tungsten	<0.1-0.3(14)	0.00(3)	0.2(3)	n/a
Vanadium	<0.1-0.7(14)	0.01-0.1(2,3)	0.07-0.22(3,7)	n/a
Zirconium	0.1-0.3(14)	0.02-0.07(2,3)	0.1(3)	n/a
Major/minor gangue				
Aluminium	40-95(14)	2.5-35.5(2,3,4)	8.2-102(3,7)	77-80.5(13)
Calcium	0.6-53.3(1,14)	1.4-14(1, 2,3,4,5)	2.5-61(1,3,7)	20.7-37.8(13)
Magnesium	0.2-30(14)	0.15-12(2,3,4,5)	2.5-26(3,7)	7.6-12.4(13)
Potassium	1-87(14)	0.3-14(2,3)	3.7-56(3,7)	39-56(13)
Silica	210-350(1,14)	8-170(1, 2,3,4,5)	180-302(1,3)	281-350(10,13)
Sodium	6-37(14)	0.07-13.9(2,3)	<0.1-13(3,7)	8.2-17(13)
Minor/trace gangue				
Barium	0.05-5(14)	<0.04-0.3(2)	0.1-1(3,7)	<5.4(13)
Chloride	n/a	0.1(3)	2.4(3)	n/a
Fluoride	n/a	0.1-0.2(3)	<0.005(3)	n/a
Strontium	0.8(14)	0.01-0.38(2,3)	<0.1(3)	n/a

Mineralogical compositions

Mineral	Run-of-mine ore (%)	Concentrates (%)	Tailings (%)	Waste rock (%)
Major copper sulphide ore minerals				
Chalcopyrite:$CuFeS_2$	22.6(12)	3-83(2,6)	0.29-1.1(12)	<0.1-0.8(10)
Bornite: Cu_5FeS_4	n/a	7-10(2)	n/a	n/a
Chalcocite: Cu_2S	n/a	1-46(2,6)	n/a	<0.3(10)
Total	22.6(12)	23-84(2,6)	n/a	<0.1-0.8(10)
Iron sulphide ore minerals				
Pyrite: FeS_2	49(12)	3-36(2,6,12)	1-55(7,12)	3.3-4(10)
Pyrrhotite: FeS	n/a	0-1(2)	n/a	n/a
Total	49(12)	3-36(2,6,12)	n/a	n/a
Other minor sulphide ore minerals				
Molybdenite: MoS_2	n/a	0-2(2)	n/a	n/a
Sphalerite: ZnS	1.09(12)	0-3.13(2,12)	n/a	n/a
Galena: PbS	n/a	0-1(2)	n/a	n/a
Enargite: Cu_3AsS_4	n/a	<1(2)	n/a	n/a
Tetrahedrite: $(CuFe)_{12}Sb_4S_{13}$	0.54(12)	0-2(2,12)	0.03-0.24(12)	n/a
Tennanite: $(CuFe)As_4S_{13}$	1.14(12)	0-3(2,12)	0.58-0.68(12)	n/a
Bismutite: Bi_2S_3	n/a	0-1(2)	n/a	n/a
Arsenopyrite: $FeAsS_2$	n/a	<1(2)	n/a	n/a
Stibnite: Sb_2S_3	n/a	<1(2)	n/a	n/a
Stannite: Cu_2FeSnS_4	0.67(12)	0-1.7(2,12)	0.07(12)	n/a
Acanthite: Ag_2S	n/a	<1(2)	n/a	n/a
Total	3.44(12)	2-4(2)	n/a	n/a
Minor non-sulphide ore minerals				
Iron oxides (magnetite, goethite)	n/a	0-8(2)	n/a	n/a
Sphene: $CaTiSiO_5$	n/a	0-1(2)	n/a	n/a
Ilmenite: $FeTiO_3$	n/a	<1(2)	n/a	n/a
Wolframite: $(Fe,Mn)WO_4$	n/a	0-1(2)	n/a	n/a
Electrum: AuAg	n/a	<1(2)	n/a	n/a
Total	n/a	0-8(2)	n/a	n/a
Silicate gangue minerals				
Quartz: SiO_2	n/a	10-27(2,6)	n/a	29-68(10)
K-Al-silicates	n/a	10-22 (2,6)	n/a	4-40(10)
Total	n/a	10-49(2,6)	n/a	72(10)
Carbonate gangue minerals				
Ankerite: $Ca(Fe,Mg)(CO_3)_2$	n/a	<0.5(2,6)	n/a	n/a
Calcite: $CaCO_3$	n/a	<0.5(2,6)	n/a	n/a
Siderite: $FeCO_3$	n/a	<1(2,6)	n/a	n/a
Dolomite: $CaMg(CO_3)_2$	n/a	0-2(2,6)	n/a	n/a
Total	n/a	0-4(2,6)	0.2-8(9)	<0.1-8(9)

References:

1. Ayres et al. (2002) ; 2. Private Communications, BHP Billiton Technology Centre, Johannesburg (1995-1997); 3. Private communications with Cresta, Department of Chemical Engineering, University of Sydney.(2002); 4. Biswas & Davenport (1994); 5. Dreisinger (2003); 6. King et al. (1993); 7. Dold & Fontbote (2001); 8. Aso et al. (1984); 9. Seal & Foley (2002); 10. Murr et al. (1981); 11. Bulatovic (1997); 12. Benzaazoua et al. (2002); 13. Strőmberg & Banwart (1999); 14. du Bray (1996); 15. Brzezicka & Baranowska, I.(2001); 16. Rubenstein & Barsky (2002); 17. Hansen et al. (2005). 18. Bulatovic et al. (1998)

E3 Base-metal sulphide tailings deposits

Particle size distribution of fresh base metal sulphide tailings

Tailings deposit description	Particle size	References
9A	48% -74µm 80% -214µm	Bulatovic et al. (1998)
9B	40% -74µm 80% -320µm	As above
9C	46% -74µm 80% -180µm	As above
9D	52% -74µm 80% -160µm	As above
9E	55% -74µm 80% -140µm	As above
9F	50% -74µm 80% -160µm	As above
10	10% -2.26µm 50% -38.5µm 90% -166µm	Coetzer et al. (2003)

Compositions of tailings discharge waters

Property	Unit	Tailings deposit 10 (Coetzer et al., 2003)	Tailings deposit 11 (Ng'andu, 2001)	Tailings deposit 7 Mwale et al., 2005)
pH		8.5	10.5	11.3
TDS	ppm	949	2055	2028
Total hardness	ppm $CaCO_3$	-	1692	-
Ca	ppm	45	653	-
Mg	ppm	72	36	-
Na	ppm	120	n/a	-
K	ppm	24		-
sulphate	ppm	309	1363	1989
nitrate	ppm	15	-	-
Cl	ppm	183	-	4
CN	ppm	53	-	-
Si	ppm	2.3	-	-
Cu	ppm	17.2	1.6	0.3
Zn	ppm	0.34	0.1	<0.01
Pb	ppm	0.33	0.5	0.1
Ag	ppm	0.03	-	-
Fe	ppm	0.09	1.1	0.3
Mn	ppm	0.16	-	0.29
Ni	ppm	0.34	-	-
Ba	ppm	0.22	-	-
Sr	ppm	0.48	-	-

The chemical composition of pore waters in tailings impoundments

	Surface zones			Oxidation zones							
Parameter*	Deposit 1 (Carlsson, 2003)	Deposit 2 (Al et al., 2000)	Deposit 3 (Van Huyssteen, 1998)	Deposit 1 (Carlsson, 2003)	Deposit 2 (Al et al., 2000)	Deposit 4 (Patinha et al., 2004)	Deposit 5 (Benner et al., 2000)	Deposit 3 (Van Huyssteen, 1998)	Deposit 6A (Kontopoulos et al., 1995)	Deposit 6B (Kontopoulos et al., 1995)	Deposit 6C (Kontopoulos et al., 1995)
pH	3.4	3.9	3.6	3.2	4.4	3.6	3.5	4.2	2.5	2.3	4
Redox (mV)	550	621	459		621	-	450	415	520	420	-
TDS	3460	27390	-	7918	32113	-	-	-	-		-
Ca	370	452	426	370	458	-	-	461	500	400	500
Mg	44	3000	1938	145	3550	-	-	2158	1000	2200	700
Na	343	69	20	12	110	-	-	23	-	-	-
K	19	40	12	3	70	-	-	24	-	-	-
sulphate	2409	21400	24489	5466	22900	-	3700	26802	15500	50000	1000
Cl	-	16	-	-	28	-	-	-	-	-	-
carbonate	-	-	-	-	-	-	-	-	-	-	-
Cu	0.64	2.2	0.06	0.04	2.2	-	-	0.04	-	-	-
Fe	122	19	4395	1512	0.7	2606	600	7886	300	3200	80
Zn	80	1430	852	192	4080	-	-	7.7	5000	1300	40
Pb	0.008	1.1	0.09	0.3	2.3	-	-	0.007	1	2.5	2.5
As	0.003	-	0.07	-	0.02	0.2	-	0.03	-	-	-
Mo	-	-	-	-	-	-	-	-	-	-	-
Cd	0.09	43	1.01	0.64	54	-	-	0.05	20	6	-
Si	30	28	49	45	40	-	-	19	-	-	-
Al	34	-	1212	158	5.5	-	-	55	-	-	-
Mn	7	877	55	11	811	-	-	80	-	-	-
Sr	0.3	-	-	0.2	-	-	-	-	-	-	-
Cr	0.003	-	4.6	0.3	-	-	-	0.11	-	-	-
Ni	0.6	7	20	1	8	-	-	-	-	-	-
Co	0.9	-	26	1.8	-	-	-	0.9	-	-	-
Ba	-	-	34	-	-	-	-	44	-	-	-
V	-	-	0.09	-	-	-	-	0.02	-	-	-

* All values except pH and redox potential in ppm

	Transition zones		Unoxidised zones					
Parameter*	Deposit 2 (Al et al., 2000)	Deposit 3 (Van Huyssteen, 1998)	Deposit 1 (Carlsson, 2003)	Deposit 2 (Al et al., 2000)	Deposit 4 (Patinha et al., 2004)	Deposit 5 (Benner et al., 2000)	Deposit 6B (Kontopoulos et al., 1995)	Deposit 3 Van Huyssteen, 1998)
pH	6.8	5.7	4.2	6.6	5.8	4.9	7	6.8
redox	217	359	-	165	-	350	330	354
TDS	13999	-	3459	7299	-	-	-	-
Ca	440	447	153	369	-	-	200	307
Mg	1780	1964	117	317	-	-	300	131
Na	720	70	8	160	-	-	-	97
K	86	64	4	67	-	-	-	42
sulphate	10080	21894	2229	5580	-	3700	1000	1440
Cl	54	-	-	16	-	-	-	-
carbonate	-	-	-	-	-	5	-	-
Cu	0.07	0.06	0.004	-	-	-	-	0.03
Fe	254	6243	465	388	-	600	-	32
Zn	421	1.3	361	388	-	-	4	<0.1
Pb	0.3	0.007	0.2	0.2	-	-	-	0.003
As	0.05	-	0.1	0.02	<0.02	-	-	<0.1
Mo	-	-	-	-	-	-	-	-
Cd	54	-	0.04	0.8	-	-	0.05	-
Si	21	11	6	10	-	-	-	11
Al	-	3.3	110	-	-	-	-	0.1
Mn	87	68	5.4	2.7	-	-	-	0.6
Sr	-	-	0.2	-	-	-	-	-
Cr	-	0.009	0.22	-	-	-	-	<0.009
Ni	1.1	0.7	0.2	0.06	-	-	-	-
Co	-	0.04	0.16	-	-	-	-	0.02
Ba	-	56	-	-	-	-	-	237
V	-	-	-	-	-	-	-	0.02

* All values except pH and redox potential in ppm

	Ground interface zone					
Parameter*	Deposit 1 (Carlsson, 2003)	Deposit 2 (Al et al., 2000)	Deposit 3 (Van Huyssteen, 1998)	Deposit 7 (Mwale et al., 2005)	Deposit 8 (Komitsas, 1998	Deposit 5 (Benner et al., 2000)
pH	5.7	7	7.8	7.1	5.8	6
redox	-	94	456	-	303	150
TDS	2903	4521	-	-	-	-
Ca	444	451	97	-	106	-
Mg	45	175	26	-	24	-
Na	8	105	68	-	-	-
K	3	22	16	-	-	-
sulphate	1935	3740	48	1989	-	3200
Cl	-	16.2	-	5	-	-
carbonate	-	-	-	-	-	54
Cu	0.002	-	0.02	0.3	-	-
Fe	419	8	1	0.3	-	1300
Zn	42	0.2	0.3	<0.1	0.06	-
Pb	0.0005	-	0.007	0.1	-	-
As	0.002	0.02	-	-	-	-
Mo	0.0004	-	-	-	-	-
Cd	0.0004	-	-	-	5.02	-
Si	4	3	7	-	-	-
Al	0.05	-	0.2	-	-	-
Mn	2.5	1.3	0.2	0.3	-	-
Sr	0.3	-	-	-	-	-
Cr	0.0006	-	0.01	-	-	-
Ni	-	-	-	-	-	-
Co	-	-	0.02	-	-	-
Ba	-	-	385	-	-	-
V	-	-	0.02	-	-	-

* All values except pH and redox potential in ppm

Description of Tailings:

Deposit 1: Kristinberg pyrite rich Cu- Zn tailings (Carlsson et al., 2003): 14.4 % S; 9% Zn; 0.1% Cu and 17% Fe with minor calcite

Deposit 2: Kidd Creek pyrite rich Zn-Cu tailings (Al et al. 2000): 10-20% pyrite; 8% carbonate minerals; 1% each of sphalerite, chalcopyrite and pyrrhotite:

Deposit 3: Flotation tailings from a pyrrhotite rich Cu-Zn-Ag ore (van Huyssteen, 1998): 11% S; 27% Fe; 0.25 Cu; 1.2 % Zn and 123 ppm As. Sulphides comprised mainly of pyrrhotite (30 mass %) and lithophilic gangue of Cs-Mg-Fe silicates. Carbonates < 0.5%.

Deposit 4: Talhadas pyrite rich Cu-Pb-Zn tailings with minor As (Patinha et al., 2004).

Deposit 6: Pyrite rich Pb-Zn tailings (Kontopoulos et al., 1995):

A Kavodokanos : 5-10% S; 16% pyrite; Fe 5-17%; Zn 0.5-3%

B: 2-5% S; 9% pyrite; 3-15% Fe; 0.5-5 % Zn

C Bodossakis: 10-32% S; 43% pyrite; 18-28% Fe and 0.5-1.2% Zn

Deposit 5: Nickel Rim pyrrhotite rich Cu-Ni tailings (Benner et al., 2000): 13.6% S

Deposit 7: KCM Konkola copper sulphide tailings (Mwale et al., 2005): 0.5-1% Cu.

Deposit 8: Baia copper sulphide tailings (Komitsas et al., 1998): 3% S; 7% Fe; 0.07 % Cu, paste

pH 2.4. Non-sulphide gangue comprised mainly of quartz.

Deposit 9: Porphyry Cu-Mo sulphide tailings (Bulatovic et al. 1998): 1-6 % pyrite; 4-6% Fe; Cu: 0.2-0.5%; Zn: 40-300 ppm; Mo 60-230 ppm. Carbonates < 1.4%

A: El Salvador

B: Chuquicamata

C: El Teniente

D: Disputada

E: El Cobre

F: Andina

Deposit 10: Rosh Pinah Pb-Ag-Cu sulphide tailings (Coetzer et al., 2003): 9% spaherite, 2% galena; 03% chalcopyrite and 7% pyrite. Non-sulphide gangue is mainly quartz (40 mass %) and dolomite (33.4%)

Deposit 11: ZCCM Mufulira copper sulphide tailings (Ng’andu, 2001)

APPENDIX F

PREDICTING PHYSIO-CHEMICAL CHARACTERISTICS OF PORPHYRY-TYPE COPPER SULPHIDE ORES AND TAILINGS

F1 Predicting concentrations and distributions of major mineral groups and associated elements for the ore → tailings system: mass balance calculations

1. $C_{\text{m,conc}}$(kg/t)

Mass balance equation	Assumptions
$C_{\text{Fe,conc}} = (0.304\ C_{\text{chalcopyrite, conc}} + 0.466\ C_{\text{pyrite, conc}} + 0.1113\ C_{\text{bornite, conc}})/0.85$ $C_{\text{S,conc}} = (0.349\ C_{\text{chalcopyrite, conc}} + 0.534\ C_{\text{pyrite, conc}} + 0.2552\ C_{\text{bornite, conc}} + 0.2011\ C_{\text{chalcocite, conc}})/0.96$ $C_{\text{Cu,conc}} = (0.347\ C_{\text{chalcopyrite, conc}} + 0.6334\ C_{\text{bornite, conc}} + 0.7988\ C_{\text{chalcocite, conc}})/0.99$ $C_{\text{gangue,conc}} = 1000 - (C_{\text{chalcopyrite, conc}} + C_{\text{pyrite ,conc}} + C_{\text{bornite, conc}} + C_{\text{chalcocite, conc}} + C_{\text{minor-trace metal minerals, conc}})$ $C_{\text{silicate minerals,conc}} = (0.9 \text{ to } 0.98)\ C_{\text{gangue,conc}}$ $C_{\text{carbonate \& oxide minerals, conc}} = C_{\text{gangue,conc}} - C_{\text{silicate minerals,conc}}$ $C_{\text{quartz,conc}} = 0.45 C_{\text{silicate minerals, conc}}$ $C_{\text{K-feldpar,conc}} = 0.25 C_{\text{silicate minerals, conc}}$ *m: biotite, muscovite and albite* $C_{\text{m,conc}} = 0.10 C_{\text{silicate minerals, conc}}$ $C_{\text{calcite,conc}} = 0.70\ C_{\text{carbonate minerals, conc}}$ *m: dolomite, ankerite and siderite* $C_{\text{m,conc}} = 0.10 C_{\text{carbonate minerals, conc}}$ $C_{\text{si}} = (0.47\ C_{\text{quartz,conc}} + 0.162\ C_{\text{biotite, conc}} + 0.197\ C_{\text{feldspar,conc}} + 0.222\ C_{\text{albite,conc}} + 0.211\ C_{\text{muscovite,conc}})/0.98$ $C_{\text{Al}} = (0.156\ C_{\text{biotite, conc}} + 0.190\ C_{\text{feldspar,conc}} + 0.214\ C_{\text{albite,conc}} + 0.204\ C_{\text{muscovite,conc}})/0.98$ $C_{\text{K}} = (0.075\ C_{\text{biotite, conc}} + 0.275\ C_{\text{feldspar,conc}} + 0.098 C_{\text{muscovite,conc}})/0.98$ $C_{\text{Na}} = (0.183\ C_{\text{albite,conc}})/0.98$ $C_{\text{Mg}} = (0.07\ C_{\text{biotite, conc}} + 0.13\ C_{\text{dolomite,conc}})/0.98$ $C_{\text{Ca}} = (0.4\ C_{\text{calcite,conc}} + 0.217\ C_{\text{dolomite, conc}} + 0.345\ C_{\text{ankerite, conc}})/0.98$	• The major copper and iron sulphide minerals occur as chalcopyrite (20-70%), pyrite (5-35%), bornite (1-8%) and chalcocite (1-18%) • These minerals account for 99% of the total copper, 95% of the total sulphur , and 85% of the total iron in the concentrate. • Total concentration of minor and trace metal bearing minerals varies from 2-8% • Copper/sulphide ratios are approximately 1.2/1 (after Ayres et al., 2002) • The majority of the non-sulphide gangue is comprised of silicate minerals (90-98% of total gangue), of which 45% is present as quartz, 25% as K-feldspar and 10% each of biotite , albite and muscovite. • The remaining gangue is made up of oxides (< 8%) and carbonates (< 4%), of which 70% is in the form of calcite together with 10% each of ankerite, siderite and dolomite • The listed gangue minerals account for 98% of the Si, Al, K, Mg, Na and Ca in the concentrate

2.$C_{m,ore}$ (kg/t)

Mass balance equation	Assumptions
m = chalcopyrite, bornite, chalcocite, pyrite, minor/trace metal minerals, copper $C_{m,conc}/(M_{t,ore} \times D_{m, conc})$ *m = Fe* $(0.304\ C_{chalcopyrite, ore} + 0.466\ C_{pyrite, ore} + 0.1113\ C_{bornite, ore})/0.96$ *m = S* $(0.349\ C_{chalcopyrite, ore} + 0.534\ C_{pyrite, ore} + 0.2552\ C_{bornite, ore} + 0.2011\ C_{chalcocite, ore})/0.96$ *m = gangue* $1000 - (C_{chalcopyrite, ore} + C_{pyrite, ore} + C_{bornite, ore} + C_{chalcocite, ore} + C_{minor\text{-}trace\ metal\ minerals, ore})$ *m = silicates, carbonates, Si, Al, Ca, Mg, K, Na* $(C_{m,conc} \times C_{gangue, ore} \times M_{t,ore})$ $/(M_{t,ore} \times C_{gangue, conc})$	$M_{t, ore}$ (t ore/ t conc.)= $M_{t, tails}$ +1 $D_{copper\ minerals, conc}$ = 0.85-0.9 $D_{Cu, conc}$ = 0.85-0.9 $D_{pyrite, conc}$ = 0.05-0.1 $D_{minor\text{-}trace\ metal\ minerals, conc}$ = 0.7-0.9

3. $D_{m,conc}$

Mass balance equation	Assumptions
m = Fe, S, gangue $C_{m,conc}/(C_{m, ore} \times M_{t,ore})$ *m = silicates, carbonate, Si, Al, Ca, Mg, K, Na* $D_{gangue, conc}$	

4. $C_{m, tails}$ (kg/t)

Mass balance equation	Assumptions
$((C_{m, ore} \times M_{t,ore}) - C_{m,conc})/ M_{t, tails}$	$M_{t, tails}$ (t tails/ t conc.)= 37

5. $D_{m, waste\ rock}$

Mass balance equation	Assumptions
m = chalcopyrite, bornite, chalcocite, pyrite, minor/trace metal minerals, Fe and S $(C_{Cu, waste\ rock} \times M_{t,waste\ rock}) /(M_{t,ore} \times C_{Cu, ore})$ *m = gangue, silicates, carbonates, Si, Al, Ca, K, Mg, Na* $(C_{gangue, waste\ rock} \times M_{t, waste\ rock})/(C_{gangue, ore} \times M_{t,ore})$	$C_{Cu, waste\ rock}$ = 1.5-2 kg/t $M_{t,waste\ rock}$ (t waste rock/t conc.)= $M_{t ,tails} \times 1.9$ $C_{gangue, waste\ rock}$: Calculated (point 6)

6. $C_{m,\text{ waste rock}}$

Mass balance equation	Assumptions
m = chalcopyrite, bornite, chalcocite, pyrite, minor/trace metal minerals, Fe and S, silicates, carbonates, Si, Al, Ca, Mg, K, Na $(D_{m,\text{ waste rock}} \times C_{m,\text{ ore}} \times M_{t,\text{ ore}}) / M_{t,\text{waste rock}}$ *m = gangue* $1000 - (C_{\text{chalcopyrite, waste rock}} + C_{\text{pyrite, waste rock}} + C_{\text{bornite, waste rock}} + C_{\text{chalcocite, waste rock}} + C_{\text{minor-trace metal minerals, waste rock}})$	

Where:

- $C_{m,x}$ = concentration of substance *m* in stream *x*
- $D_{m,x}$ = (mass substance *m* in stream *x)* / (mass of substance *m* in the ROM ore)
- $M_{t,\,x}$ = (total mass of stream *x)* / (mass of concentrate)

F2 Predicting concentrations and speciation of distributions of individual elements in copper sulphide ROM ores and tailings streams.

Mass balance calculations

Mass balance equation	Assumptions
1. Empirical enrichment factors in ores for element m $(E_{m, tailings})_{empirical} = (C_{m, ore})_{empirical} / C_{m, crust}$ 2. Predicted element enrichment factors in tailings for element m $E_{m, tailings} = (E_{m, ore} \times D_{m, tailings})$ 3. Predicted concentration ranges for element m Ore concentrations: $C_{m, ore} = (E_{m, ore} \times C_{m, crust})$ Tailings concentrations: $C_{m, tailings} = (D_{m, tails} \times C_{m, ore}) / (1-(1/ M_{t ,ore}))$	• Available empirical concentrations for elements in typical porphyry-type copper sulphide ores are taken from du Bray (1996) and Bulatovic (1998) –See Appendix 6.1. • Average crustal abundance concentrations values ($C_{m, crust}$) are based on Beus & Grigorian (1977); Cotton & Wilkinson (1962); Cox (1995) – See Appendix 2.2. • Between 99.4 and 99.7 % of the gangue elements in the ROM ore deport to the tailings: i.e. $D_{gangue\ elements, tails} = 0.994$ to 0.997 • Between 10 and 15% of the copper in the ROM ore reports to the tailings: i.e. $D_{Cu, tails} = 0.10$ to 0.15 • Between 63% and 93% of the Fe and S in the ROM ore reports to the tailings: i.e. $D_{Fe\ \&\ S, tails} = 0.63\text{-}0.93$ • Between 10 and 30% of trace to minor chalcophiles and siderophiles in the ROM ore report to the tailings: i.e. $D_{m, tails} = 0.10\text{-}0.$ • Approximately 37 tons of tailings are produced per ton of concentrate from 38 tons of ore: i.e. $M_{t, tails}$ (t tails/ t conc.)= 37 and $M_{t,ore}$ (t ore/ t conc.)= 38

Where:

- $C_{m,x}$ = concentration of substance *m* in stream *x*
- $D_{m,x}$ = (mass substance *m* in stream *x)* / (mass of substance *m* in the ROM ore)
- $M_{t, x}$ = (total mass of stream *x)* / (mass of concentrate)
- $E_{m,x}$ = (mass substance *m* in stream *x)* / (average mass of substance *m* in the earth's crust)

Appendix F2

Predicted element speciation in copper sulphide ores, tailings and concentrates

Element	Major mineral phases	Trace/minor mineral phases
Major rock forming gangue minerals:		
Si	• Quartz (SiO_2) • *Al-silicates:* 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 ($(MgFe)_5Al(Si_3Al)O_{10}(OH)_8$)	• *Secondary Al-silicates*: kaolinite ($Al_2Si_2O_5(OH)_4$); pyrophyllite ($Al_2Si_4O_{10}(OH)_2$); topaz ($Al_2SiO_4(F,OH)_2$) • *Calc-alkaline silicates*: amphiboles ($Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$); epidote ($Ca_2(Fe,Al)_3(SiO_4)_3(OH)$); anorthite: $CaAl_2Si_2O_8$; stilbite: $CaNa_2K_2Al_2Si_{17}O_{18}$ • *silicates of trace/minor gangue elements* such as Ti, Zr, Cr, B, Be.
Al	*Al-silicates*: as for Si	• *Secondary Al-silicates:* kaolinite, pyrophyllite, topaz and alunite ($K_2Al_6(SO_4)_4(OH)_{12}$) • *Calc-alkaline silicates:* epidote, anorthite, stilbite • *Minor/trace silicate minerals* of elements such as B (tourmaline)
K	*Al-silicates:* K-feldspar; biotite, muscovite	*Al-gangue minerals*: stilbite; alunite
Na	*Al-silicates:* albite	*Al-silicate minerals*: stilbite
Ca	*Carbonates:* calcite ($CaCO_3$); dolomite ($CaMg(CO_3)_2$); ankerite $(CaFe)_{0.5}CO_3$	• anhydrite ($CaSO_4$) • *Calc-alkaline silicate minerals*: epidote; anorthite; stilbite • *Minor/ trace gangue minerals* of P (apatite); F (fluorite); Ti (sphene); W (scheelite)
Mg	• *Carbonates*: dolomite • *Al-silicates*: biotite and chlorite	• *Calc-alkaline silicates*: amphiboles; • *Trace-mineral gangue minerals* of elements such as Cr (chromite).
Major sulphide ore minerals :		
Iron	*Iron sulphides*. pyrite (FeS_2) >> marcasite (FeS_2) > pyrrhotite (FeS)	• *Carbonates*: ankerite; siderite ($FeCO_3$) • *Fe-oxides*: magnetite (Fe_3O_4); haematite (Fe_2O_3) • *Al-silicates*: biotite; chlorite; muscovite • *Minor/ trace gangue minerals* of elements such as Cr (chromite); W (wolframite) and B (tourmaline)
Sulphur	Iron sulphides	• *Copper sulphide minerals* • *Trace/minor sulphide minerals* of elements such as As, Zn, Pb, and Mo. • *Sulphate gangue minerals* of elements such as Ca (anhydrite); Ba (barite)and Al (alunite)
Cu	*Copper sulphide minerals*: chalcopyrite ($CuFeS_2$) > bornite (Cu_5FeS_4), > chalcocite (Cu_2S)	*Copper sulphide minerals*: tetrahedrite ($(CuFe)_{12}Sb_4S_{13}$) >covellite (CuS)

Element	Major mineral phases	Trace/minor mineral phases
Other sulphide ore forming elements		
Zn	*Zinc sulphide mineral* : sphalerite (ZnS)	
Pb	galena (PbS)	
As	arsenopyrite (FeAsS)	• *Copper sulphide minerals*: tennanite ((CuFe)As_4S_{13})> enargite (Cu_3AsS_4) • Inclusions in pyrite
Mo	molybdenite (MoS_2)	
Se	selenides of Cu, Ag & Au	
Sb	terahedrite ($(CuFe)_{12}Sb_4S_{13}$)	stibnite (Sb_2S_3)
Ge	dispersed in sphalerite	
Ni	• pentlandite ($(Fe, Ni)_9S_8$) • dispersed in pyrite	
Bi	• bismutite (Bi_2S_3) • native bismuth • dispersed in galena	
Co	• cobaltite (CoAsS) • dispersed in pyrite	
Cd	• greenocktite (CdS) • dispersed in sphalerite	
Ag	• electrum (AuAg) • acanthite/Argentite (Ag_2S)	
PGMs (mainly Pt, Pd)	dispersed in sulphides	
Hg	dispersed in galena	cinnabar (HgS)
In	dispersed in sphalerite	
Au	• native Au • Au telluride • electrum AuAg	
Re	dispersed in molybdenite	
Te	tellurides of Cu, Au and Ag.	
Tl	dispersed in galena	

Element	Major mineral phases	Trace/minor mineral phases
Other lithophilic gangue minerals:		
P	apatite ($Ca_5(PO_4)_3(F, Cl. OH)$)	monazite ($(Ce, Th, La)PO_4$),
Ba	barite ($BaSO_4$)	
Ti	sphene ($CaTi(SiO_4)$)	Other Ti silicates and oxides such as Ilmenite & rutile
F	fluorite (CaF_2)	apatite
Mn	carbonate: ($MnCO_3$);	• *Mn-oxides*: pyrolusite • *carbonate minerals*: ankerite • *trace/minor gangue minerals* of elements such as W (wolframite)
Sr, Rb	dispersed in rock forming minerals	
Zr	zircon ($ZrSiO_4$)	
Cl, Li	dispersed in rock forming minerals	
REE (rare earths)	monazite ($(Ce, Th, La)PO_4$),	*dispersed in Ti minerals* such as sphene
V	dispersed in sphene?	
Cr	chromite ($FeMgCr_2O_4$)	
B	tourmaline ($NaFe_3Al_6(BO_3)Si_6O_{18}(OH)_4$	
Sn	cassiterite (SnO_2)	
Nb	columbite-tantalite ($(Ta, Nb)_2O_6$)	
Ga	dispersed in quartz?	
W	wolframite ($(Fe, Mn)WO_4$), scheelite ($CaWO_4$)	
Be	beryl ($Be_3Al_2Si_6O_{18}$)	
Hf	dispersed in zircon	
Sc, Br	dispersed in rock forming minerals	
U	uraninite (UO_2)	
Ta	columbite-tantalite ($(Ta, Nb)_2O_6$)	
I	Dispersed in rock forming minerals	

APPENDIX G

SCREENING ENVIRONMENTALLY SIGNIFICANT CHARACTERISTICS OF PORPHYRY-TYPE COPPER SULPHIDE TAILINGS

G1: Prediction of generic hazard and risk potential factors for porphyry-type copper sulphide tailings in a disposal scenario

Hazard potential factors

Component	Predicted concentration range (ppm)	Crustal abundance (ppm)	Typical guidelines for drinking water (ppm)	Hazard potential factors/1000	
				Minimum	Maximum
As	2-550	1.8	0.01	<0.11	17236
Cd	0.2-60	0.2	0.005	<0.1	3600
Mo	2-450	1.5	0.05	<0.1	2846
Ag	0.1-20	0.07	0.01	<0.01	630
Al	40000-100000	81300	0.2	100	615
Fe	8000-90000	50000	0.1	4	602
Se	1-30	0.09	0.02	0.6	426
Sb	0.2-60	0.2	0.05	<0.01	384
S	10000-110000	520	83	2.3	279
Si	210000-350000	277200	5*	59	87
Mn	100-2000	1000	0.05	0.2	84
Pb	5-100	16	0.01	<0.1	61
Cu	80-1300	55	1	12	31
B	50-1000	10	0.3	<0.1	21
Bi	0.2-60	0.2	1*	<0.01	19
F	60-3000	600	1	<0.01	15
REE	10-870	85	1*	<0.01	9
Sn	15-300	3	5*	<0.1	6
Te	0.01-0.5	0.001	0.02*	<0.01	5
Hg	0.02-0.6	0.08	0.001	<0.01	5
Ti	400-9000	4400	5*	<0.01	4
Ba	45-880	430	0.7	<0.01	3
Be	1-30	2.8	0.1*	<0.01	3
W	5-100	1	5*	<0.01	2
Zn	15-500	80	3	<0.01	1
Ni	1-50	75	0.02	<0.01	1
Cr	10-200	100	0.5	<0.01	1
Ca	4000-45000	36300	100*	<0.01	1
Tl	0.06-2	0.3	0.02*	<0.01	1
P	100-6100	1200	5*	<0.01	1
Pt	0.01-2	0.005	1*	<0.01	0.5
Zr	50-500	100	5*	<0.01	0.5
K	3000-35000	28300	100*	<0.01	0.4
Na	3000-32000	25900	100	<0.01	0.4
Mg	2000-26000	20900	100*	<0.01	0.3
Re	<0.01-0.5	0.001	1*	<0.01	0.25
V	15-300	150	5*	<0.01	0.12

Hazard potential factors continued….

Component	Predicted concentration range (ppm)	Crustal abundance (ppm)	Typical guidelines for drinking water (ppm)	Hazard potential factors/1000	
				Minimum	Maximum
U	1-10	1.5	1*	<0.01	0.07
In	0.01-0.5	0.07	0.05*	<0.01	0.07
Nb	10-200	19	30*	<0.01	0.07
Au	0.002-1.2	0.004	5*	<0.01	0.07
Ge	0.5-10	1.3	1*	<0.01	0.05
Rb	10-600	120	100	<0.01	0.03
Cl	50-500	100	100	<0.01	0.03
Li	15-300	30	100*	<0.01	0.03
Ga	2-80	15	30*	<0.01	0.01
Sr	30-600	290	100*	<0.01	0.01
Hf	0.5-30	2.6	30*	<0.01	0.009
Co	0.3-15	25	1*	<0.01	0.009
Sc	1-70	14	100*	<0.01	0.004
Ta	0.1-10	1	30*	<0.01	0.003
Br	0.5-30	2.5	100*	<0.01	0.003
I	0.05-5	0.5	30*	<0.01	0.002

Crustal abundance values are sourced from Cotton & Wilkinson (1962) and Cox (1995)

Drinking water values are sourced from ANZECC (1999) and DWAF (1996)

*Quantitative drinking water quality guidelines are not available for these elements-limits have been estimated on the basis of available data and general information pertaining to chemical and toxicological properties.

Risk potential factors

Component	Reactivity factors for primary phases			Net availability factors		
	Reactivity potential factors	Reactive concentration range (ppm)	Associated risk potential factor/1000	Availability potential factors	Available concentration range (ppm)	Associated risk potential factor//1000
As	0.9-0.95	<1-530	<0.01-15556	<0.01-0.02	<0.01-10	<0.01-6
Cd	0.9-0.95	<1-60	<0.1-3249	0.15-0.6	0.03-37	<0.01-1372
Mo	0.9-0.95	1-440	<0.1-2568	<0.01-0.02	<0.01-8	<0.01-1
Ag	0.9-0.95	<1-20	<0.1-569	<0.01	≤0.02	<0.01
Fe	0.75-0.95	5850-90250	2-543	<0.01-3	<0.01-2800	<0.01-0.5
Se	0.9-0.95	1-30	<0.5-385	<0.01-0.05	≤0.01	<0.01-1
Sb	0.9-0.95	<1-60	<0.01-347	≤0.03	<0.01-2	<0.01-0.3
S	0.9-0.95	9000-110000	2-252	0.7-0.9	7200-102400	1.2-242
Mn	0.75-0.95	2050	<0.1-76	0.6-0.9	60-1850	0.06-70
Pb	0.9-0.95	3-100	<0.01-55	≤0.01	≤1	<0.01
Al	0.1-0.3	4100-30000	1-55	≤0.01	0.01-300	<0.01
Cu	0.9-0.95	720-1240	9-28	≤0.1	0.01-120	≤0.2
Bi	0.9-0.95	<1-60	<0.01-17	≤0.02	≤1	<0.01
F	0.4-0.6	25-1840	<0.01-6	≤0.06	0.5-180	≤0.05
Te	0.9-0.95	≤0.5	<0.01-4	≤0.01	<0.01	<0.01
Hg	0.9-0.95	≤0.5	0.01-4	≤0.01	<0.01	<0.01
B	0.1-0.3	5-300	0.01-2	0.1-0.3	5-300	<0.01-2
Ni	0.9-0.95	1-40	<0.01-1.3	0.15-0.7	0.1-30	<0.01-0.7
W	0.-0.6	2-60	<0.01-0.8	<0.01	≤0.06	<0.01
Zn	0.9-0.95	15-479	<0.01-0.9	0.5-0.76	7-370	<0.01-0.6
REE	0.1-0.3	1-260	<0.01-0.8	n.d.	n.d.	n.d.
Sn	0.1-0.3	2-90	<0.01-0.5	n.d.	n.d.	n.d.
Tl	0.9-0.95	<1-2	<0.01-0.5	n.d.	n.d.	n.d.
Ca	0.5-0.8	2000-36000	<0.01-0.4	0.3-0.8	1200-36000	<0.01-0.4
Ti	0.1-0.3	1-60	<0.01-0.3	n.d.	n.d.	n.d.
Ba	0.1-0.3	5-260	<0.01-0.2	<0.01	≤0.3	<0.01
Si	0-0.05	<1-350000	<0.01-0.2	<0.05	<0.01-17400	≤0.2
Be	0.1-0.3	<1-9	<0.01-0.3	n.d.	n.d.	n.d.
P	0.4-0.6	40-3700	<0.01-0.2	n.d.	n.d.	n.d.
Mg	0.5-0.8	1000-20800	<0.010.2	0.5-0.8	950-20800	≤0.2
Ge	0.9-0.95	≤8	<0.01-<0.1	0.9-0.95	0.3-8	≤0.04
Cr	0.1-0.3	1-60	<0.01-<0.1	n.d.	n.d.	n.d.
K	0.1-0.3	300-10500	<0.01-<0.1	≤0.3	<0.01-10500	≤0.04
Na	0.1-0.3	300-9500	<0.01-<0.1	≤0.3	<0.01-9500	≤0.03
Re	0.9-0.95	≤0.5	<0.01-<0.1	n.d.	n.d.	n.d.
V	0.1-0.3	2-90	<0.01-<0.1	n.d.	n.d.	n.d.
U	0.4-0.6	≤5	<0.01-<0.1	n.d.	n.d.	n.d.
In	0.9-0.95	≤0.5	<0.01-<0.1	n.d.	n.d.	n.d.
Nb	0-0.05	≤10	<0.01	n.d.	n.d.	n.d.
Au	0-0.05	≤0.05	<0.01	n.d.	n.d.	n.d.
Pt	0-0.05	≤2	<0.01	n.d.	n.d.	n.d.
Zr	0-0.05	<1-26	<0.01	n.d.	n.d.	n.d.
Rb	0.1-0.3	1-180	<0.01	n.d.	n.d.	n.d.
Cl	0.1-0.3	1-150	<0.01	n.d.	n.d.	n.d.

Risk potential factors continued…..

Component	Reactivity factors for primary phases			Net availability factors		
	Reactivity potential factors	Reactive concentration range (ppm)	Associated risk potential factor/1000	Availability potential factors	Available concentration range (ppm)	Associated risk potential factor//1000
Li	0.1-0.3	2-90	<0.01	n.d.	n.d.	n.d.
Ga	0.1-0.3	<0.01-20	<0.01	n.d.	n.d.	n.d.
Sr	0.1-0.3	3-180	<0.01	n.d.	n.d.	n.d.
Hf	0-0.05	≤1	<0.01	n.d.	n.d.	n.d.
Co	0.9-0.95	<0.01-14	≤ 0.01	n.d.	n.d.	n.d.
Sc	0.1-0.3	<0.01-0.2	<0.01	n.d.	n.d.	n.d.
Ta	0-0.05	≤1	<0.01	n.d.	n.d.	n.d.
Br	0.1-0.3	<0.01-8	<0.01	n.d.	n.d.	n.d.
I	0.1-0.3	≤ 2	<0.01	n.d.	n.d.	n.d.

Reactive concentrations (ppm) = reactivity potential factor x total element concentration in solid tailings (ppm)

Available concentrations (ppm) = availability potential factor x total element concentration in solid tailings (ppm)

Associated risk potential factors = (reactive or available concentrations in solid tailings (ppm))^2 x crustal abundance (ppm)x typical water quality guideline limits (ppm)

Where: total element concentrations in solid tailings, crustal abundance and typical water quality values are presented in the previous table.

n/d = not determined

G2: Prediction of reactivity potential factors for primary phases within porphyry-type copper sulphide tailings impoundments

Qualitative description of the predicted thermodynamic stability of primary minerals in typical copper sulphide tailings within the oxidation and transitional zone (based on Brookins, 1988; Ďuďa & Rejl, 1986; Garrels, 1960; Thornton, 1983)

Thermodynamic stability	Mineral description	Associated elements
Unstable	Sulphide minerals	As, Cu, Fe, Pb, Se, Cd, Se, Mo, Sb, Te, Ag, Bi, Zn, Ge, Hg.
	carbonates calcite, ankerite, siderite , dolomite, rhodocrosite	Ca, Mg, (Mn)
Partially stable	*Simple and complex oxides:* wolframite/scheelite; uranninite; the oxides of Mn; Fe oxides (goethite and haematite); apatite.	W, U, P, (Mn), (Fe), F
Stable	*Acid insoluble silicates* Al silicates (biotite, chlorite, feldspar and albite); calc-alkaline silicates (amphibole, epidote); beryl; tourmaline; sphene	Al, K, Na, Ba, (Mg), (Fe), (Si) , Be, B, Ti, Cl, Li, Rb, V, Sr
	Acid insoluble oxides monazite; cassiterite/stannite; chromite	REE, Sn, Cr, (Fe)
	Metals	PGMs, Au
Inert	Quartz, zircon, columbite/tantalite	(Si), Ta, Nb, Zr, Hf.
Where: Elements in brackets are indicative of minor to partial associations with mineral phases in this group.		

Reported results from sequential chemical extraction tests on tailings from the unoxidised tailings impoundment zones (Carlsson et al., 2002; Dold & Fontbote, 2001)

	Residual fraction (% of total)		Reactive fraction (% of total)	
	Range	Arithmetic mean	Range	Arithmetic mean
Highly reactive (> 90%)				
Cu	0.7-14	4.1	86-99	95.9
S	0	0	100	100
Zn	0-21	9.1	79-100	90.9
Pb	0-16	4.1	84-100	95.9
As	0-36	9.0	64-100	91.0
Mo	0-12	5. 3	88-100	94.7
Cd	0	0	100	100
Ni	0	0	100	100
Reactive (75-95%)				
Fe	6-25	16.0	76-94	84.0
Mn	10-24	15.9	76-90	84.1
Cr	11-22	16.7	78-89	83.3
Partially reactive (50-80%)				
Ca	15-50	30.0	50-85	70.0
Mg	31-39	35.4	62-69	64.6
Relatively unreactive (5%-50%)				
Al	70-89	83.5	11-30	16.5
K	85-97	92.5	3-16	7.5
Na	77-96	86.7	4-23	13.3
Ti	53-100	75.8	0-46	24.2
V	49-76	60.7	24-51	39.3
Ba	73-83	78.3	17-27	21.7
Inert (<5%)				
Si	97	96.5	3.5	3.5
Where: Only that fraction of an element remaining in the residual phase is considered inert over geographical time.				

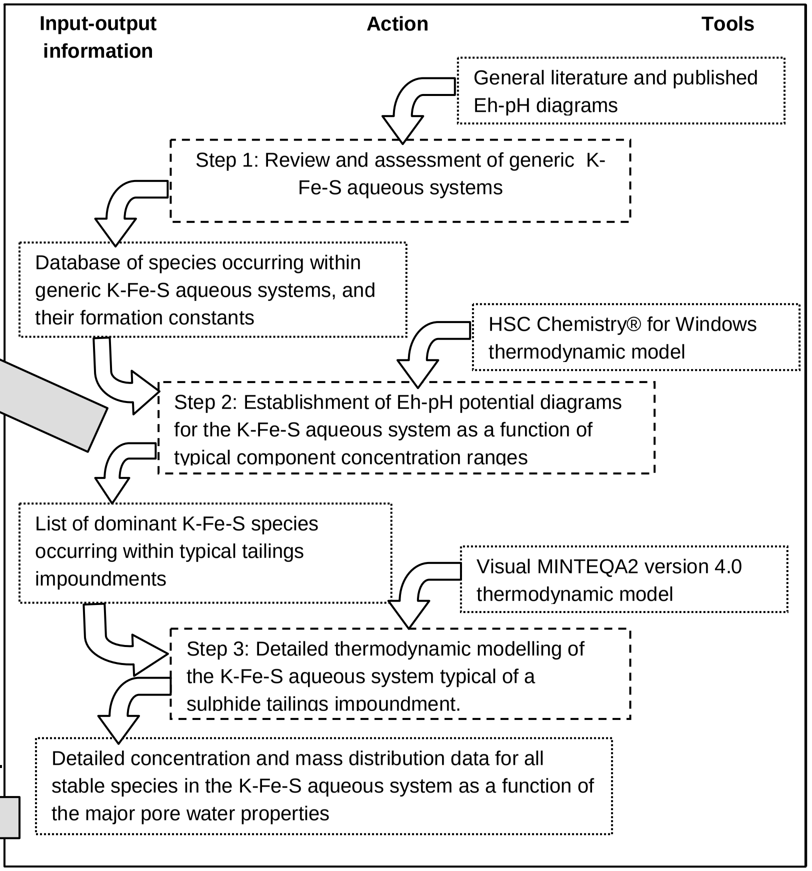
G3: Prediction of attenuation potential factors for soluble elements within porphyry-type copper sulphide tailings impoundments: Thermodynamic modelling

Model input parameters

pH	Redox potential (mV)		pH	Redox potential (mV)	
	min	max		min	max
Oxidation zone			***Transitional-unoxidised zone***		
2.5	550	650	4.5	220	340
3	520	620	5	200	320
3.5	490	590	5.5	170	290
4	460	560	6	150	270
4.5	430	530	6.5	120	250
			7	100	220

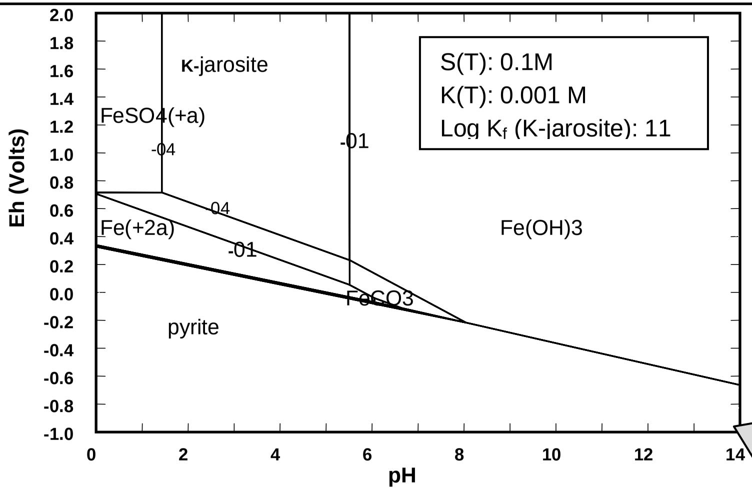
Element	Concentration range (ppm)
calcium	350-500
magnesium	100-1000
potassium	10-100 (40)
sodium	10-100
sulphate	5000-25000
carbonate	5-100 (50)
iron	100-1000 (500)
zinc	100-1000
manganese	50-500 (100)
molybdenum	50-500
aluminium	4-400 (40)
boron	10-200
arsenic	50-150
lead	10-100
cadmium	10-100
nickel	10-100
copper	5-100
silica	10-40
barium	5-10
antimony	5-10
germanium	5-10
bismuth	5-10
tungsten	5-10

Predictive thermodynamic modelling of the potential extent of attenuation and speciation of iron within a typical sulphide tailings impoundment



Input-output information	Action	Tools
		General literature and published Eh-pH diagrams
	Step 1: Review and assessment of generic K-Fe-S aqueous systems	
Database of species occurring within generic K-Fe-S aqueous systems, and their formation constants		
		HSC Chemistry® for Windows thermodynamic model
	Step 2: Establishment of Eh-pH potential diagrams for the K-Fe-S aqueous system as a function of typical component concentration ranges	
List of dominant K-Fe-S species occurring within typical tailings impoundments		
		Visual MINTEQA2 version 4.0 thermodynamic model
	Step 3: Detailed thermodynamic modelling of the K-Fe-S aqueous system typical of a sulphide tailings impoundment.	
Detailed concentration and mass distribution data for all stable species in the K-Fe-S aqueous system as a function of the major pore water properties		

e.g.



e.g.

	Concentration	Activity
Fe(OH)2 (aq)	1.69E-18	1.71E-18
Fe(OH)2+	1.02E-05	8.57E-06
Fe(OH)3-	2.05E-26	1.71E-26
Fe(OH)3 (aq)	1.5E-12	1.52E-12
Fe(OH)4-	1.13E-17	9.51E-18
Fe(SO4)2-	0.000163	0.000135
Fe+2	0.010694	0.005391
Fe+3	0.000187	4.87E-05
Fe2(OH)2+4	5.76E-06	3E-07
Fe3(OH)4+5	5.91E-08	5.83E-10
FeOH+	8.14E-10	6.8E-10
FeOH+2	0.0003	0.000146
FeSO4 (aq)	0.004431	0.004502
FeSO4+	0.003527	0.002946
H+1	0.003673	0.003162
HSO4-	0.001264	0.001051
K+1	9.42E-09	7.72E-09
KOH (aq)	4.21E-20	4.25E-2
KSO4-	2.22E-10	1.86E-1

Fe(T): 10 00 ppm; S(T): 10 000 ppm
K(T): 1000 ppm; pH: 2.5; Eh: 650 mV

	% of total	Species name
Fe+2	70.71	Fe+2
	29.29	FeSO4 (aq)
K+1	97.70	K+1
	2.30	KSO4-
SO4-2	43.28	SO4-2
	20.96	FeSO4+
	1.93	Fe(SO4)2-
	7.51	HSO4-
	26.33	FeSO4 (aq)
Fe+3	4.46	Fe+3
	83.99	FeSO4+
	3.87	Fe(SO4)2-
	7.15	FeOH+2

Solids	Conc (M)
K-Jarosite	2.56E-2
Schwertmannite	4.36E-3

Component	Total Dissolved	% dissolved	Total precipitated	% precipitated
Fe+2	0.015	100	0	0
Fe+3	0.004	2.56	0.16	97.44
H+1	0.0046	100	0	0
K+1	9.64E-09	0	0.026	100
SO4-2	0.017	16.17	0.09	83.83

APPENDIX H

EMPIRICAL CHARACTERISATION OF A PORPHYRY-TYPE COPPER SULPHIDE TAILINGS SAMPLE: SCE AND ACID GENERATING TEST METHODS

H1: Sequential chemical extraction testwork

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.

- 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

- 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.

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

- Step 3: 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.

H2: Acid generating capacity testwork

Fizz rating for ABA test methods

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.

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

Standard Sobek ABA test

- Digestion method for standard Sobek ANC test
    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.

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.

- 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

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

- Digestion method for Skousen H_2O_2 ANC test
  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

- 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% H2O2, 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

Incremental H_2O_2 Addition ABA test

- Digestion method

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

- Back titration for Incremental H_2O_2 Addition 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.

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:
  1. Sodium Hydroxide (NaOH) – 0.10 M and 0.50 M

2. 15 % v/v H_2O_2.

- Notes:

1. H_2O_2 should be at room temperature before commencing the test.
2. 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

- Procedure:

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.

Sequential NAG test

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

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).

Calculation methods of the ANC, NAPP and NAG

Test method	Equation
NAPP (Net Acid Production Potential)	NAPP = MPA - ANC
MPA (Maximum Potential Acidity)	MPA = wt% total x 30.6 (total S determined by LECO)
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.
H_2O_2 siderite correction ANC test (Skousen *et al.*, 1997)	As for Standard Sobek ANC test in kg H_2SO_4/t
Additional/Incremental H_2O_2 ANC method	As for Standard Sobek ANC test in kg H_2SO_4/t
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).

APPENDIX I

SCREENING ENVIRONMENTALLY SIGNIFICANT CHARACTERISTICS OF A PORPHYRY-TYPE COPPER SULPHIDE TAILINGS SAMPLE ON THE BASIS OF EMPIRICAL CHARACTERISATION TESTWORK

Hazard potential

Component	Empirical concentrations (ppm)	Crustal abundance (ppm)	Typical guidelines for drinking water (ppm)	Hazard potential factors/1000
Fe	71536	50000	0.1	341
As	27.9	1.8	0.01	43
Si	232882	277200	5*	39
Mn	1244	1000	0.05	31
Cu	1169	55	1	25
S	28000	520	83	18
Mo	25.5	1.5	0.05	9
Pb	36	16	0.01	8
Ni	109.2	75	0.02	8
Ag	1.5	0.07	0.01	3
Sb	5	0.2	0.05	2
Cd	1.4	0.2	0.005	2
Al	4986	81300	0.2	1.5
Cr	270	100	0.5	1.5
K	13128	28300	100*	0.06
Zn	118	80	3	0.06
Ca	9099	36300	100*	0.02
Co	19	25	1*	0.01
Mg	3202	20900	100*	0.005
Be	1	2.8	0.1*	0.004
V	37	150	5*	0.002
Se	n.d.	0.09	0.02	0

Crustal abundance values are sourced from Cotton & Wilkinson (1962) and Cox (1995)

Drinking water values are sourced from ANZECC (1999) and DWAF (1996)

*Quantitative drinking water quality guidelines are not available for these elements-limits have been estimated on the basis of available data and general information pertaining to chemical and toxicological properties.

Risk potential

Element	Reactivity factors for primary phases in the oxidation zone			Availability factors on the basis of attenuation			Availability on the basis of reaction of primary factors in the unoxidised zone		
	Reactivity potential factors	Reactive concentration range (ppm)	Associated risk potential factor/1000	Availability potential factors	Available^1 concentration range (ppm)	Associated risk potential factor//1000	Solubility potential factors	Availble^2 concentration range (ppm)	Associated risk potential factor//1000
Fe	0.53-0.79	3791-56513	96-213	<0.01-0.3	0-1695	0-0.2	0.004-0.008	286-2269	<0.01-0.3
As	0.39-0.53	11-15	7-12	<0.01-0.02	0-0.3	<0.01	0	0-0.03	<0.01
Si	0.07-0.08	16302-18631	0.2	<0.05	n.d.	0.2-0.3	n.d..	n.d.	n.d.
Mn	0.67-0.88	833-1095	14-24	0.6-0.9	625-1095	8-24	0.18	849-1319	14-35
Cu	0.98-1.0	1146-1169	24-25	<0.01	0-117	0-0.2	0.1-0.11	117-245	0.2-1
S	0.98-1.0	2740-28000	17-18	0.7-0.9	21952-28000	11-18	0	21952-28000	11-18
Mo	0.84-0.94	21-24	6-7	<0.01-0.02	0-0.5	<0.01	0	0-0.5	<0.01
Pb	0.83-0.92	30-33	6-7	<0.01	0-0.3	<0.01	0.08	2.9-3.2	0.05-0.06
Ni	0.94-1.0	103-109	7-8	0.15-0.7	15-82	0.2-4.5	0.09-0.11	25-94	0.4-6
Ag	0.88-0.91	1	2-3	<0.01	0-0.01	<0.01	0	0-0.01	<0.01
Sb	0.90-0.95	4	1.6-2	<0.03	0-0.13	<0.01	0	0-0.13	<0.01
Cd	0.96-1.0	1	1.7-2	0.15-0.6	0.2-0.9	0.04-0.8	0.4-0.5	0.7-1.6	0.5-2.4
Al	0.15-0.23	78-1147	0.03-0.1	<0.01	0-12	<0.01	0	0-12	<0.01
Cr	0.71-0.9	191-254	0.7-1.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
K	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ca	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Co	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mg	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Be	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
V	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Se	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Reactive concentrations (ppm) = reactivity potential factor x total element concentration in solid tailings (ppm)

[1] Available concentrations (ppm) = availability potential factor x total element concentration in solid tailings (ppm)

[2] Available concentrations (ppm) = [1] Available concentrations (ppm) + (solubility potential factor x total element concentration in solid tailings (ppm))

Associated risk potential factors = (reactive or available concentrations in solid tailings (ppm))^2 x crustal abundance (ppm)x typical water quality guideline limits (ppm)

APPENDIX J

DERIVATION OF A MODIFIED SHRINKING CORE MODEL FOR PYRITE OXIDATION

The leachate generation model developed for copper sulphide tailings differs from the standard shrinking core model derived above in a number of key ways. This model considers:

- Two liquid phase regions – a static liquid phase and a dynamic liquid phase – and a partially wetted particle surface. The standard shrinking core model assumes a thin liquid film surrounds the particles.
- Oxygen mass transport from the bulk gas directly to the dynamic liquid and the particle pores (through the non-wetted surface) and indirect dissolved oxygen transport (controlled by a mass transfer coefficient) from the dynamic liquid phase to the static liquid phase. In contrast, the standard shrinking core model assumes that oxygen in the bulk gas phase is in equilibrium with the single liquid phase.
- Ferrous ion oxidation described by abiotic and biotic reaction kinetics occurring in both the dynamic and static liquid regions at a rate determined by the concentrations of reactants in these phases. The standard shrinking core model considers instantaneous ferrous ion oxidation occurring at the reaction front.
- Sulphide oxidation occurs via shrinking core kinetics with separate terms for sulphide oxidation by dissolved oxygen and sulphide oxidation by ferric ion. In contrast, the standard shrinking core model only has a term for pyrite oxidation by dissolved oxygen and a factor to account for the stoichiometric differences between the two oxidants based on bulk conditions and the local equilibrium assumption.
- Pyrite and chalcopyrite oxidation are accounted for

The specific model assumptions are:

- Spherical sulphide mineral particles of radius, R, are surrounded by static and dynamic liquid regions with a non-wetted portion of solid surface in contact with the bulk gas phase.
- The driving force for the diffusion of oxygen to the reaction front (and thus the rate of reaction) is the oxygen concentration gradient between the surface of the particle (at R) and the reaction front (where it is assumed that the dissolved oxygen concentration is zero).
- This concentration gradient will vary depending on the phase or region in contact with the surface (i.e. static liquid, dynamic liquid, bulk gas).
- Therefore, three different rates can be identified and the overall rate can be calculated by summing these rates weighted according to the fraction of surface covered by each region.

It is further assumed that pyrite oxidation is not only limited to an oxygen-controlled reaction process. The presence of ferric ion is significant in determining the overall rate of pyrite oxidation and it therefore needs to be modelled explicitly. To achieve this it is assumed that:

- Ferrous ion oxidising bacteria (e.g. *Thiobacillus ferrooxidans*) is present in the liquid surrounding the particles or attached to the external particle surface.
- Ferrous ion oxidation occurs kinetically in the static and dynamic liquid regions according to abiotic or biotic reaction kinetics and the prevailing environmental conditions (e.g. pH, dissolved oxygen concentration etc.).
- The driving force for pyrite oxidation by ferric ion is assumed to be limited by the diffusion of ferric ion to the reaction front and can be described according to shrinking core kinetics where diffusion of the reactant to the reaction site controls.

- The rate of pyrite oxidation by ferric ion is then determined by the concentration gradient between the particle surface (at R) and at the reaction front, where the concentration of ferric ion is assumed to be zero.
- The concentration gradient varies depending on the region in contact with the surface. Note that for the surface fraction exposed to the bulk gas phase the rate is zero.
- Therefore, two different rates can be identified and the overall rate calculated by summing these rate terms weighted according to the fraction of surface covered by each region.

For pyrite oxidation by dissolved oxygen, the derivation of the oxygen consumption term according to shrinking core kinetics, detailed above, is still valid. Thus equation J1 holds.

$$Q_{O_2} = \frac{3D_w(1-\theta_b)}{R^2}\frac{r_c}{R-r_c}C_{s,O_2} \tag{J1}$$

Except here, the concentration of oxygen at the surface, C_{s,O_2}, will change based on the phase in contact with the particle surface and the fraction of surface area covered by that particular phase. Thus for the static liquid phase covering a fraction, f_{st}, of the particle surface, the oxygen consumption term becomes:

$$Q_{O_2} = \frac{3D_w(1-\theta_b)}{R^2}\frac{r_c}{R-r_c}f_{st}C_{st,O_2} \tag{J2}$$

Similarly, for the dynamic liquid phase covering a fraction, f_d, of the particle surface, the oxygen consumption term is:

$$Q_{O_2} = \frac{3D_w(1-\theta_b)}{R^2}\frac{r_c}{R-r_c}f_dC_{d,O_2} \tag{J3}$$

And for the bulk gas phase, where the fraction of surface area is (1-f):

$$Q_{O_2} = \frac{3D_w(1-\theta_b)}{R^2}\frac{r_c}{R-r_c}(1-f)\frac{C_{g,O_2}}{H} \tag{J4}$$

Source terms for reaction products are then proportional to the oxygen concentration sink term according to the reaction stoichiometry. As reaction products cannot be added to the bulk gas phase, the reaction products resulting from pyrite oxidation by dissolved oxygen from the non-wetted surface are added to the static liquid and dynamic liquid phase in proportion to the particle surface area they cover.

The shrinkage of reaction front as a result of pyrite oxidation by oxygen is then given by:

$$\frac{dr_c}{dt} = -\frac{D_w(1-\theta)}{\varepsilon\rho_s}\frac{R}{r_c(R-r_c)}\left(f_{st}C_{ts,O_2} + f_dC_{d,O_2} + (1-f)\frac{C_{g,O_2}}{H}\right) \tag{J5}$$

here ε is simply the mass ratio of oxygen to sulphur consumed based on the stoichiometry of reaction J6 and adjusted by the molar mass of oxygen to account for the fact that concentrations in this model are molar.

$$FeS_2 + H_2O + \tfrac{7}{2}O_2 \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{J6}$$

Pyrite oxidation by ferric ion occurs in accordance with reaction J7.

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{J7}$$

In this case the driving force for pyrite oxidation by ferric ion is the rate of diffusion of ferric ion, which is proportional to the ferric ion concentration gradient between the outside surface of the particle $C_{s,Fe^{3+}}$ and at the reaction front where $C_{p,Fe^{3+}} = 0$. The steady state assumption allows the rate of consumption of oxygen by a single pyrite-containing particle to be expressed as the rate of diffusion to the reaction surface, so that:

$$\frac{dM_{Fe^{3+}}}{dt} = -4\pi r^2 q_{Fe}{}^{3+} \qquad J8$$

where $q_{Fe}{}^{3+}$ is the inward flux of ferric ion through the surface of the particle, which may be expressed in the form of Fick's Law as:

$$-q_{Fe^{3+}} = D_f \frac{dC_{p,Fe^{3+}}}{dr} \qquad J9$$

where D_f is an effective diffusion coefficient describing the diffusion of ferric ion from the liquid phase in contact with the particle to the reaction front within the particle.
Substitution of J8 into J9 with rearrangement yields:

$$\frac{dM_{Fe^{3+}}}{dt}\frac{dr}{r^2} = 4\pi D_f dC_{p,Fe^{3+}} \qquad J10$$

Integrating across the oxidised shell from R to r_c results in the mass rate of change per particle:

$$\frac{dM_{Fe^{3+}}}{dt}\int_{r_c}^{R}\frac{1}{r^2}dr = 4\pi D_f \int_{0}^{C_{s,Fe^{3+}}} dC_{p,Fe^{3+}} \qquad J11$$

$$\frac{dM_{Fe^{3+}}}{dt} = 4\pi D_f \frac{Rr_c}{R-r_c} C_{s,Fe^{3+}} \qquad J12$$

To obtain the mass rate of consumption of ferric ion per unit volume of porous material requires multiplication by the number of particles, n_p, to obtain

$$Q_{Fe^{3+}} = \frac{3D_f(1-\theta_b)}{R^2}\frac{r_c}{R-r_c}C_{s,Fe^{3+}} \qquad J13$$

Where,

$$n_p = \frac{3(1-\theta)}{4\pi R^3} \qquad J14$$

The rate of change of the unreacted core radius, r_c, can be obtained from the relationship between the masses of ferric ion and sulphur consumed. Here the mass changes of $Fe3^+$ and S are related by ε_f, which is the mass ratio of ferric ion to sulphur consumed based on stoichiometry of reaction represented by J7.

$$dM_{Fe^{3+}} = \varepsilon_f dM_s \qquad J15$$

The mass of sulphur in the particle, M_s, can in turn be related to the particle radius according to:

$$M_s = \frac{\rho_s}{(1-\theta)}V_s \qquad J16$$

$$V_s = \tfrac{4}{3}\pi r^3 \qquad J17$$

$$M_s = \frac{4}{3}\frac{\rho_s \pi r^3}{(1-\theta)} \qquad J18$$

Here ρ_s is the density of sulphur in the particle and the product of bulk density, ρ_b, and the fraction of sulphur present in the waste material, f_s.

The mass rate of change of sulphur in the particle can then be related to the rate of change in radius:

$$dM_s = -\frac{4\pi\rho_s}{(1-\theta)} r_c{}^2 dr_c \qquad J19$$

Rearrangement of and substitution of equation J13 and J15 gives the rate of change of the unreacted particle core as a function of the ferric ion concentration at the surface of the particle.

$$\frac{dr_c}{dt} = -\frac{D_f(1-\theta)}{\varepsilon_f \rho_s} \frac{R}{r_c(R-r_c)} C_{s,Fe^{3+}} \qquad J20$$

The consumption of ferric ion in the static and dynamic liquid regions is then given by equations J21 and J22 respectively.

$$Q_{Fe^{3+}} = \frac{3D_f(1-\theta_b)}{R^2} \frac{r_c}{R-r_c} f_{st} C_{st,Fe^{3+}} \qquad J21$$

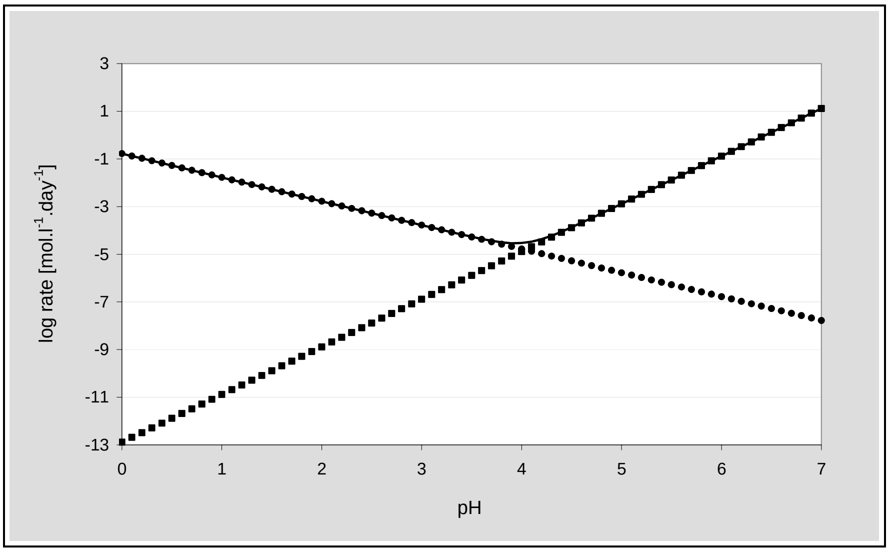
$$Q_{Fe^{3+}} = \frac{3D_f(1-\theta_b)}{R^2} \frac{r_c}{R-r_c} f_d C_{d,Fe^{3+}} \qquad J22$$

Similarly, the rate of change of the unreacted core is given by:

$$\frac{dr_c}{dt} = -\frac{D_f(1-\theta)}{\varepsilon_f \rho_s} \frac{R}{r_c(R-r_c)} (f_{st} C_{st,Fe^{3+}} + f_d C_{d,Fe^{3+}}) \qquad J23$$

Incorporation of ferrous ion oxidation kinetics

The static and dynamic liquid regions also require terms to account for abiotic and biotic ferrous ion oxidation. The body of the report briefly described the incorporation of existing laboratory determined rate expressions. It was noted that these literature rate expressions are only valid over certain pH ranges. If these pH ranges are included in the model using conditional if statements (or the like) to determine when they are applied, computational difficulties arise. To overcome these difficulties brought about by the discontinuities during transition between valid rate expressions a smoothed or continuous rate expression was needed. In this case, the pH dependent rate expressions of Stumm and Morgan (1981) and Kirby *et al.* (1999) provided a simple solution to smoothing which would be acceptable at this stage of model development. As the biotic rate law of Kirby *et al.* (1999) decreases with increasing pH and the abiotic rate increases with increasing pH and both expressions are negligible when the other is dominant, summing the two rate expressions resulted in a continuous rate expression. Figure J1 shows the log of the abiotic and biotic rate and the resulting smoothed rate when these rates are summed.



FigureJ1: To obtain the 'smoothed' ferrous ion oxidation rate function the abiotic rate (directly proportional to pH) and the biotic rate (inversely proportional to pH) are summed

The reaction terms in the static and dynamic liquid regions are then in the static liquid:

$$\sum R = \theta_s(s_{i,abiotic}k_{abiotic}\frac{C_{st,Fe^{2+}}C_{st,O_2}}{(C_{st,H^+})^2} + s_{i,biotic}k_{biotic}C_{st,Fe^{2+}}C_{st,O_2}C_{st,H^+}C_{bact}) \tag{J24}$$

And the dynamic liquid:

$$\sum R = \theta_d(s_{i,abiotic}k_{abiotic}\underset{\text{abiotic rate}}{\frac{C_{d,Fe^{2+}}C_{d,O_2}}{(C_{d,H^+})^2}} + s_{i,biotic}k_{biotic}C_{d,Fe^{2+}}C_{d,O_2}C_{d,H^+}C_{bact}) \tag{J25}$$

Adding these sink/source and reactive terms to the generic model equations presented in Appendix C, yields the following set of dimensionless equations describing 1-D transport and reaction in a bed of pyrite-containing particles:

In the bulk gas phase:

$$\theta_g\frac{\partial C_{g,O}}{\partial t} = \frac{\theta_g D_a}{H^2}\frac{\partial^2 C_{g,O_2}}{\partial z^2} - a_g\frac{(C_g - H_cC_{d,O_2})}{\left(\frac{1}{k_g}\right)+\left(\frac{H_c}{k_L}\right)} - \frac{3D_w(1-\theta_b)}{R_p^{\,2}}\frac{r_c}{(1-r_c)}(1-f)\frac{C_{g,O_2}}{H_c} \tag{J26}$$

Accumulation = bulk diffusion - mass transfer from bulk gas phase - consumption from non-wetted surface (shrinking core O_2)
Conditions: if $r_c > 0$ only transport terms apply

In the dynamic liquid phase:

For dissolved oxygen:

$$\begin{aligned}\theta_d\frac{\partial C_{d,O}}{\partial t} &= \frac{\theta_d D_L}{H^2}\frac{\partial^2 C_{d,O_2}}{\partial z^2} - \frac{u}{H}\frac{\partial C_{d,O_2}}{\partial z} - k_{a,O_2}(C_{d,O_2} - C_{st,O_2})\\ &+ a_g\frac{(C_g - H_cC_{d,O_2})}{\left(\frac{1}{k_g}\right)+\left(\frac{H_c}{k_L}\right)} - \frac{3D_w(1-\theta_b)}{R_p^{\,2}}\frac{r_c}{(1-r_c)}f_dC_{d,O_2} + \theta_d(-\tfrac{1}{4})k_{r,abiotic}\frac{C_{d,Fe^{2+}}C_{d,O_2}}{(C_{d,H^+})^2}\\ &+ \theta_d(-\tfrac{1}{4})k_{r,biotic}C_{d,Fe^{2+}}C_{d,O_2}C_{d,H^+}C_{bact}\end{aligned} \tag{J27}$$

Accumulation = dispersion/diffusion - advection - mass transfer to static region + mass transfer from bulk gas phase - consumption from dynamic region (shrinking core O_2) + "generation" via abiotic and biotic ferrous ion oxidation
Conditions: if $r_c > 0$ only transport and non-shrinking core reaction terms apply

For ferrous ion (Fe^{2+}):

$$\begin{aligned}\theta_d \frac{\partial C_{d,Fe^{2+}}}{\partial t} &= \frac{\theta_d D_L}{H^2}\frac{\partial^2 C_{d,Fe^{2+}}}{\partial z^2} - \frac{u}{H}\frac{\partial C_{d,Fe^{2+}}}{\partial z} - k_{a,Fe^{2+}}(C_{d,Fe^{2+}} - C_{st,Fe^{2+}})\\ &+ \frac{2}{7}\frac{3D_w(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)} f_d C_{d,O_2} + \frac{2}{7}\frac{f_d}{f}\frac{3D_w(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)}(1-f)\frac{C_g}{H_c}\\ &+ \frac{15}{14}\frac{3D_f(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)} f_d C_{d,Fe^{3+}} + \theta_d(-1)k_{r,abiotic}\frac{C_{d,Fe^{2+}}C_{d,O_2}}{(C_{d,H^+})^2}\\ &+ \theta_d(-1)k_{r,biotic}C_{d,Fe^{2+}}C_{d,O_2}C_{d,H^+}C_{bact}\end{aligned} \tag{J28}$$

Accumulation = dispersion/diffusion - advection - mass transfer to static region + generation from dynamic region (shrinking core O_2) + generation from non-wetted surface (shrinking core O_2) + generation from dynamic liquid (shrinking core Fe^{3+}) + "generation" via abiotic and biotic ferrous ion oxidation

Conditions: if r_c > 0 only transport and non-shrinking core reaction terms apply

For sulphate (SO_4^{2-}):

$$\begin{aligned}\theta_d \frac{\partial C_{d,SO_4^{2-}}}{\partial t} &= \frac{\theta_d D_L}{H^2}\frac{\partial^2 C_{d,SO_4^{2-}}}{\partial z^2} - \frac{u}{H}\frac{\partial C_{d,SO_4^{2-}}}{\partial z} - k_{a,SO_4^{2-}}(C_{d,SO_4^{2-}} - C_{st,SO_4^{2-}})\\ &+ \frac{4}{7}\frac{3D_w(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)} f_d C_{d,O_2} + \frac{4}{7}\frac{f_d}{f}\frac{3D_w(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)}(1-f)\frac{C_g}{H_c}\\ &+ \frac{2}{14}\frac{3D_f(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)} f_d C_{d,Fe^{3+}}\end{aligned} \tag{J29}$$

Accumulation = dispersion/diffusion - advection - mass transfer to static region + generation from dynamic region (shrinking core O_2) + generation from non-wetted surface (shrinking core O_2) + generation from dynamic liquid (shrinking core Fe^{3+})

Conditions: if r_c > 0 only transport terms apply

For hydrogen (H^+):

$$\begin{aligned}\theta_d \frac{\partial C_{d,H^+}}{\partial t} &= \frac{\theta_d D_{l,H^+}}{H^2}\frac{\partial^2 C_{d,H^+}}{\partial z^2} - \frac{u}{H}\frac{\partial C_{d,H^+}}{\partial z} - k_{a,H^+}(C_{d,H^+} - C_{st,H^+})\\ &+ \frac{4}{7}\frac{3D_w(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)} f_d C_{d,O_2} + \frac{4}{7}\frac{f_d}{f}\frac{3D_w(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)}(1-f)\frac{C_g}{H_c}\\ &+ \frac{16}{14}\frac{3D_f(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)} f_d C_{d,Fe^{3+}} + \theta_d(-1)k_{r,abiotic}\frac{C_{d,Fe^{2+}}C_{d,O_2}}{(C_{d,H^+})^2}\\ &+ \theta_d(-1)k_{r,biotic}C_{d,Fe^{2+}}C_{d,O_2}C_{d,H^+}C_{bact}\end{aligned} \tag{J30}$$

Accumulation = dispersion/diffusion - advection - mass transfer to static region + generation from dynamic region (shrinking core O_2) + generation from non-wetted surface (shrinking core O_2) + generation from dynamic liquid (shrinking core Fe^{3+}) + "generation" via abiotic and biotic ferrous ion oxidation

Conditions: if r_c > 0 only transport and non-shrinking core reaction terms apply

For ferric ion (Fe^{3+}):

$$\begin{aligned}\theta_d \frac{\partial C_{d,Fe^{3+}}}{\partial t} &= \frac{\theta_d D_{l,H^+}}{H^2}\frac{\partial^2 C_{d,Fe^{3+}}}{\partial z^2} - \frac{u}{H}\frac{\partial C_{d,Fe^{3+}}}{\partial z} - k_{a,Fe^{3+}}(C_{d,Fe^{3+}} - C_{st,Fe^{3+}})\\ &- \frac{3D_f(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)} f_d C_{d,Fe^{3+}} + \theta_d(+1)k_{r,abiotic}\frac{C_{d,Fe^{2+}}C_{d,O_2}}{(C_{d,H^+})^2}\\ &+ \theta_d(+1)k_{r,biotic}C_{d,Fe^{2+}}C_{d,O_2}C_{d,H^+}C_{bact}\end{aligned} \tag{J31}$$

Accumulation = dispersion/diffusion - advection - mass transfer to static region - consumption from dynamic liquid (shrinking core Fe^{3+}) + generation via abiotic and biotic ferrous ion oxidation

Conditions: if r_c > 0 only transport and non-shrinking core reaction terms apply

In the static liquid phase:

For dissolved oxygen:

$$\begin{aligned}\theta_{st}\frac{\partial C_{st,O}}{\partial t} &= -k_{a,O_2}(C_{st,O_2}-C_{d,O_2})-\frac{3D_w(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)}f_{st}C_{st,O_2}+\theta_{st}(-\tfrac{1}{4})k_{r,abiotic}\frac{C_{st,Fe^{2+}}C_{st,O_2}}{(C_{st,H^+})^2}\\ &+\theta_{at}(-\tfrac{1}{4})k_{r,biotic}C_{st,Fe^{2+}}C_{st,O_2}C_{st,H^+}C_{bact}\end{aligned}\tag{J32}$$

Accumulation = - mass transfer to dynamic region - consumption from static region (shrinking core O_2) + "generation" via abiotic and biotic ferrous ion oxidation
Conditions: if $r_c > 0$ only transport and non-shrinking core reaction terms apply

For ferrous ion (Fe^{2+}):

$$\begin{aligned}\theta_{st}\frac{\partial C_{st,Fe^{2+}}}{\partial t} &= -k_{a,Fe^{2+}}(C_{st,Fe^{2+}}-C_{d,Fe^{2+}})+\frac{2}{7}\frac{3D_w(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)}f_{st}C_{st,O_2}\\ &+\frac{2}{7}\frac{f_{st}}{f}\frac{3D_w(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)}(1-f)\frac{C_g}{H_c}+\frac{15}{14}\frac{3D_f(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)}f_{st}C_{st,Fe^{3+}}\\ &+\theta_{st}(-1)k_{r,abiotic}\frac{C_{st,Fe^{2+}}C_{st,O_2}}{(C_{st,H^+})^2}+\theta_{st}(-1)k_{r,biotic}C_{st,Fe^{2+}}C_{st,O_2}C_{st,H^+}C_{bact}\end{aligned}\tag{J33}$$

Accumulation - mass transfer to dynamic region + generation from static region (shrinking core O_2) + generation from non-wetted surface (shrinking core O_2) + generation from static liquid (shrinking core Fe^{3+}) + "generation" via abiotic and biotic ferrous ion oxidation
Conditions: if $r_c > 0$ only transport and non-shrinking core reaction terms apply

For sulphate (SO_4^{2-}):

$$\begin{aligned}\theta_{st}\frac{\partial C_{st,SO_4^{2-}}}{\partial t} &= -k_{a,SO_4^{2-}}(C_{st,SO_4^{2-}}-C_{d,SO_4^{2-}})+\frac{4}{7}\frac{3D_w(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)}f_{st}C_{st,O_2}\\ &+\frac{4}{7}\frac{f_{st}}{f}\frac{3D_w(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)}(1-f)\frac{C_g}{H_c}+\frac{2}{14}\frac{3D_f(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)}f_{st}C_{st,Fe^{3+}}\end{aligned}\tag{J34}$$

Accumulation = - mass transfer to dynamic region + generation from static region (shrinking core O_2) + generation from non-wetted surface (shrinking core O_2) + generation from static liquid (shrinking core Fe^{3+})
Conditions: if $r_c > 0$ only transport terms apply

For hydrogen (H^+):

$$\begin{aligned}\theta_{st}\frac{\partial C_{st,H^+}}{\partial t} &= -k_{a,H^+}(C_{st,H^+}-C_{d,H^+})+\frac{4}{7}\frac{3D_w(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)}f_{st}C_{st,O_2}\\ &+\frac{4}{7}\frac{f_{st}}{f}\frac{3D_w(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)}(1-f)\frac{C_g}{H_c}+\frac{16}{14}\frac{3D_f(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)}f_{st}C_{st,Fe^{3+}}\\ &+\theta_{st}(-1)k_{r,abiotic}\frac{C_{st,Fe^{2+}}C_{st,O_2}}{(C_{st,H^+})^2}+\theta_{st}(-1)k_{r,biotic}C_{st,Fe^{2+}}C_{st,O_2}C_{st,H^+}C_{bact}\end{aligned}\tag{J35}$$

Accumulation = - mass transfer to dynamic region + generation from static region (shrinking core O_2) + generation from non-wetted surface (shrinking core O_2) + generation from static liquid (shrinking core Fe^{3+}) + "generation" via abiotic and biotic ferrous ion oxidation
Conditions: if $r_c > 0$ only transport and non-shrinking core reaction terms apply

For ferric ion (Fe^{3+}):

$$\begin{aligned}\theta_{st}\frac{\partial C_{st,Fe^{3+}}}{\partial t} &= -k_{a,Fe^{3+}}(C_{st,Fe^{3+}}-C_{d,Fe^{3+}})-\frac{3D_f(1-\theta_b)}{R_p{}^2}\frac{r_c}{(1-r_c)}f_{st}C_{st,Fe^{3+}}\\ &+\theta_{st}(+1)k_{r,abiotic}\frac{C_{st,Fe^{2+}}C_{st,O_2}}{(C_{st,H^+})^2}+\theta_{st}(+1)k_{r,biotic}C_{st,Fe^{2+}}C_{st,O_2}C_{st,H^+}C_{bact}\end{aligned}\tag{J36}$$

Accumulation = - mass transfer to dynamic region - consumption from static liquid (shrinking core Fe^{3+}) + generation via abiotic and biotic ferrous ion oxidation
Conditions: if $r_c > 0$ only transport and non-shrinking core reaction terms apply

APPENDIX K

PREDICTIVE MODEL INPUT PARAMETERS

Leachate generation model

The baseline parameter values required for the copper tailings model were collated from waste characterisation data or literature sources related to copper tailings wastes.

Model parameter values for copper tailings scenarios and associated reference sources

Model parameter	Description	Units	Value	Reference
n_{comp}	number of components	-	15	Assignment as follows: 1. O_2, 2. H^+, 3. Fe^{3+}, 4. Fe^{2+}, 5. Cu^{2+}, 6. Mn^{2+}, 7. Al^{3+}, 8. SO_4^{2-}, 9. CO_3^{2-}, 10. H_4SiO_4, 11. K^+, 12. Na^+, 13. Ca^{2+}, 14. Mg^{2+}, 15. HCO_3^-
n_{carb}	number of carbonate minerals	-	3	1. Calcite - $CaCO_3$ 2. Siderite - $FeCO_3$ 3. Dolomite - $CaMg(CO_3)_2$
n_{sil}	number of silicate minerals	-	3	1. Quartz - SiO_2 2. Muscovite - $KAl_2[AlSi_3O_{10}](OH)_2$ 3. K-feldspar – $KAlSi_3O_8$
n_{rxn}	number of reactions	-	8	1. Abiotic ferrous ion oxidation 2. Biotic ferrous ion oxidation 3. Calcite dissolution 4. Siderite dissolution 5. Dolomite dissolution 6. Quartz dissolution 7. Muscovite dissolution 8. K-feldspar dissolution
θ_b	bulk porosity	-	0.45	refer to Task 7, table 3
θ_L	fraction of pore space filled with liquid	-	$0.5^* \theta_b$	Typical fluid properties of unsaturated tailings
θ_G	fraction of pore space filled with gas	-	$\theta_b – \theta_L$	
f	wetted fraction of particle surface	-	0.8	Own estimate
$k_{r,abiotic}$	Abiotic ferrous ion oxidation rate constant	$mmol.cm^{-3}.day^{-3}$	5.206×10^{-7}	Singer and Stumm (1970)
$k_{r,biotic}$	Biotic ferrous ion oxidation rate constant	$cm^6.l.mg^{-1}.mmol^{-1}.day^{-1}$	4.431×10^3	Kirby *et al.* (1999)
D_a	Oxygen diffusion coefficient through tailings	$cm^2.day^{-1}$	1.64×10^3	Gunsinger *et al.* (2006)
D_w	Oxygen diffusion coefficient through mineral grains	$cm^2.day^{-1}$	3.42×10^{-4}	Gunsinger *et al.* (2006)
D_f	Ferric ion diffusion coefficient through mineral grains	$cm^2.day^{-1}$	2.87×10^{-4}	Own estimate based on D_w and diffusivities
H	Bed height	cm	1000	Typical deposit height (Task 7, table 5)
H_c	Henry's constant	-	29.3	Gerke *et al.* (1998) lower bound, Cussler (1997) upper bound
R	Average particle radius	cm	0.005	Waste characterisation data
ρ_s	Sulphur density	$mg.cm^{-3}$	$fs\times\rho_b$	Waste characterisation data

ρ_b	Bulk density	$mg.cm^{-3}$	1550	Waste characterisation
f_s	Mass fraction of sulphur	-	0.044	Waste characterisation data
f_{sp}	Mass fraction of pyrite	-	0.042	Waste characterisation data
f_{scp}	Mass fraction of chalcopyrite	-	0.002	Waste characterisation data
a_g	Surface area of dynamic liquid in contact with gas phase	$cm^2.cm^{-3}$	calculated	Own derivation
D_i	Molecular diffusivity	$cm^2.day^{-1}$	$O_2 = 2.16$ $H^+ = 8.044$ $Fe^{3+} = 1.814$ $Fe^{2+} = 1.814$ $Cu^{2+} = 1$ $Mn^{2+} = 1$ $Al^{3+} = 1$ $SO_4^{2-} = 0.916$ $CO_3^{2-} = 0.916$ $H_4SiO_4 = 2.16$ $K^+ = 1$ $Na^+ = 1$ $Ca^{2+} = 1$ $Mg^{2+} = 1$ $HCO_3^- = 1$	H^+ and SO_4^{2-} values from Cussler (1997). Other values either calculated based on equation given in Welty *et al.* (1984) or estimated
D_l	Hydrodynamic dispersion coefficient	$cm^2.day^{-1}$	calculated	Equation given in Gerke *et al.* (1998).
K	Hydraulic conductivity	$cm.day^{-1}$	8.64	Scenario variable (1×10^{-6} $m.s^{-1}$)
dhdx	Hydraulic head gradient	$cm.cm^{-1}$	-0.15	Based on field data for tailings from Brookfield *et al.* (2006) – assumed constant
u	superficial velocity	$cm.day^{-1}$	$-K\times dhdx/\theta_l$	calculated
α_L	Dispersivity	cm	50	Gerke *et al.* (1998)
τ'	Tortuosity coefficient	-	0.5	Petersen (1998)
k_g	gas phase mass transfer coefficient	$cm.day^{-1}$	1.99×10^6	Cussler (1997)
k_L	liquid phase mass transfer coefficient	$cm.day^{-1}$	181	Cussler (1997)
v	Viscosity	$g.cm^{-1}.day^{-1}$	858.13	Welty *et al.* (1984)
C_{bact}	Concentration of bacteria	$mg.l^{-1}$	158	Kirby *et al.* (1999)

Correlations and equations to calculate mass transfer coefficients and other parameters

Parameter	Correlation or equation	Reference
k_a	$0.00051\left(\frac{u\rho}{a\mu}\right)^{0.67}\left(\frac{\rho D_i}{\mu}\right)^{0.5}(ad)^{0.4}\left(\frac{\mu g}{\rho}\right)^{1/3}$	Cussler (1997); d is nominal packing size and a is the packing area per bed volume.
a_g	$\frac{3f_d(1-\theta_b)}{(r+\delta)}$	Own derivation, where δ is the thickness of the dynamic liquid if uniformly coverage is assumed.
δ	$\left[\frac{\theta_d R^3}{f_d(1-\theta_b)}+R^3\right]^{\frac{1}{3}}-R$	Own derivation
D_l	$\alpha_L u+\theta_b\frac{D_i}{\tau'}$	Gerke *et al.* (1998)

Waste characteristics

Property	Value
Absolute density	3000 kg.m^{-3}
Bulk density	1550 kg.m^{-3}
Bulk porosity	0.45
Pyrite concentration	3.9-4.4 %
Chalcopyrite content	0.11-0.29 %
Calcite content	0.3-0.42 %
Dolomite content	0.05-0.06 %
Quartz content	51.6-54 %
K-feldspar content	9.0-10.5 %
Muscovite content	8.5-10.1 %

Groundwater flow and mass transport model

	Parameter	Value
Aquifer type		Sandstone
Aquifer dimensions	Length (West to East)	20000 m
	Breadth (North to South)	5000 m
	Depth	40 m
Flow parameters	Hydraulic gradient	0.001 m.m^{-1}
	Horizontal hydraulic conductivity	10 m.day^{-1}
	Effective porosity	0.46
	Specific yield	0.25
Dispersion parameters	Horizontal transverse dispersivity / Longitudinal dispersivity(TRPT)	1
	Vertical transverse dispersivity / Longitudinal dispersivity (TRPV)	0.1
	Longitudinal dispersivity	15 m
Chemical reaction parameters	Type of equilibrium sorption isotherm	linear
	Bulk density of the porous media in the aquifer	1295 kg.m^{-3}
	Retardation factor	8
	Distribution coefficient K_d	0.0025 m^3.kg^{-1}

Model assumptions

- A single unconfined aquifer is modelled; flow through fractures is not considered and the aquifer is assumed to be homogeneous and isotropic.
- No density effects are included and only a single liquid phase is modelled.
- Transient flow behaviour is included and a 2-D areal model is used, where the tailings deposit is represented by an area source with a time-dependent source release.
- Advection and dispersion are considered here, but chemical reaction is limited to adsorption