Generalised Strategy for Predicting Environmental Characteristics of Solid Mineral Wastes - A Focus on Copper

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"The challenge is to design and improve policies, processes and institutions to deal more effectively with societies growing demand for information, as technology is providing more information than ever before, though often in a highly random and uncoordinated fashion" The MMSD project report- Breaking New Ground (2002)

Abstract

The impacts associated with primary production of metallic and fossil minerals are significant, and these industry sectors are facing increasing pressure to improve environmental performance and contribute to development that is consistent with sustainability principles. The management of large volumes of solid wastes poses a particular problem, with the potential post-closure impacts and liabilities associated with the prolonged discharge of contaminated leachate from deposits of such wastes remaining of major concern to both regulators and industry. It is only by quantitatively characterising these impacts that we can begin to focus attention backwards in the material chain to the waste generation processes themselves, and thus identify opportunities for process improvements to minimise waste formation and to render wastes environmentally benign. Whilst recognising that knowledge of the key waste properties or characteristics is an essential and integral part of quantitative environmental impact predictions, currently available data pertaining to the characteristics of solid mineral wastes are largely incomplete and inconsistent, and the mechanisms of leachate generation poorly understood. The need to improve the way in which solid mineral wastes are characterised is driven not only by the limitations in terms of current data bases 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 early decision stages of an environmental performance assessment programme and, ultimately, project life cycle in a time and cost effective manner.

It is these shortcomings and challenges that this thesis attempts to address, through the development of a generalised and systematic strategy for predicting the environmentally significant properties of solid mineral wastes on the basis of ore characteristics (waste origins) and generating processes (waste source). The conceptual approach developed within this 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 origins), combined with knowledge of the process route from ore to waste (i.e. waste source). 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 are largely qualitative and inconsistent, and their deportment during the formation and subsequent beneficiation

of ore deposits generally less well understood. The methodology developed here entails the theoretical assessment of the potential distributions, properties and associations of these elements within ore deposits and across process unit operations, based on a fundamental understanding of the governing reaction mechanisms and influencing parameters. The theoretical data and information are subsequently reconciled 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 second step of the proposed approach entails the prediction of key characteristics relating to criteria of environmental significance. In this step the solid waste constituents, identified and quantified in the first step of the methodology, are screened and ranked in accordance with their hazardous properties and availability for release to the surrounding environment in a disposal scenario. As in the case of predictions of element distributions during ore formation and beneficiation, the theoretical assessment of the potential distribution behaviour of elements from solid wastes is underpinned by a qualitative understanding of the mechanisms and parameters governing their dissolution and attenuation within a waste deposit. Potential environmental risks associated with the various solid waste constituents are subsequently estimated and compared on the basis of their total concentrations, potential environmental availability, and inherent capacity to cause harm.

Three separate but inter-related case studies in the context of primary copper production present the key features of the developed approach and related tools. Such features pertain in particular to first-order predictions of the chemical and mineralogical compositions of porphyry-type copper sulphide ore deposits; the subsequent distribution of ore components during concentration and smelting of the run-of-mine ores; and the waste constituents of potential environmental significance within a typical flotation tailings impoundment. Apart from addressing data gaps and inconsistencies, these case studies have also served to highlight the links in the ore formation

Acknowledgements

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Finally, to my husband, Brendan, and son, Aidan. It is impossible, within the confines of this brief mention, to convey the gratitude and appreciation I feel for their support, love and seemingly endless patience. This despite the invasion of our home by piles of papers and books, as well as the distinct lack of home-cooked meals and meaningful conversations over the years. I am truly blessed-more than I could ever have hoped to be.

"A wrong decision in the assessment of the risks presented by wastes or contaminated land may have a very significant impact on the financial planning for long-term clean-up and environmental monitoring, potentially extending over decades or even centuries" Wood, 2001.

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"One key lesson gained from experience is that failure to establish a plan at the level of conceptual engineering before project operations begin makes the process more expensive, less effective in managing post-closure environmental impacts, and more likely to generate conflicts" Danielson & Nixon, 2000

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"Assessment tools will require a more systematic data collection and maintenance if they are to survive as quantification tools - The necessary shifts are from data to information and knowledge and from understanding to action" EEA, 1997

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"Disposal of wastes represents some risk to the environment. Reducing the quantities of waste requiring treatment and disposal and reducing the hazardous nature of the products, should, therefore receive the greatest effort" Waste Management Task Group of the Canadian Council of Ministers for the Environment, 1996.

Abbreviations

General text

ACMER	Australian Centre for Minerals Extension and Research
AD	Acid drainage
ANZECC	Australia and New Zealand Environment and Conservation Council
DWAF	(South African) Department of Water Affairs and Forestry
EEA	European Environmental Agency
EC	Electrical conductivity
ERA	Environmental risk assessment
GMI	Global Mining Initiative
ICMM	International Council on Mining and Metals
max	maximum
min	minimum
MMSD	Mining, Minerals and Sustainable Development (project)
n/d	not determined
OECD	Organisation for Economic Co-Operation and Development
ROM	Run-of mine (ore)
SAIMM	South African Institute of Mining and Metallurgy
SCE	Sequential chemical extraction (tests)
SETAC	Society of Environmental Toxicology and Chemistry
TDS	Total dissolved salts
UNIDO	United Nations Industrial Development Organisation
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

Units of measurement

atm	atmosphere-unit of pressure (1atm = 760 mmHg)
A	Angstrom-unit of length (1 A = 10^{-10}m)
°C	degree Celsius (centigrade)-unit of temperature
cm	centimetre-unit of length (1cm = 10mm)
g	gram-unit of mass (1g = 1000mg = 10^{-3}Kg)
K	Kelvin-unit of temperature (1K = 273 °C)
kg	kilogram-unit of mass (1kg = 1000g = 10^{-3}t)

kJ/mol	kilojoule per mole-unit of energy
m^2/s	square metre per second-unit of hydraulic conductivity
mS/m	millisiemens per metre-unit of conductivity (1mS/m = 1000 S/m)
mg	milligrams-unit of mass (1mg = 10^{-3}g)
mm	millimetre-unit of length (1mm = 10^{-3}m)
MPa	megapascals-unit of pressure (1MPa = 10^{6}Pa)
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)
t	metric ton-unit of mass (1t = 1000kg)

Nomenclature

$C_{m,x}$	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°	Gibbs free energy of formation
K_f	equilibrium formation constant
$M_{t,x}$	total unit mass of stream *x*
r	radius (ionic)
Z	ionic charge or oxidation state

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Introduction

The primary metal production and coal-based power generation industries produce large tonnages of solid waste each year, most of which is consigned to land disposal. Of major concern to both regulators and industry is the risk of prolonged environmental pollution and degradation of water sources and land, due to the discharge of contaminated leachate from these solid residues and deposits. In order to be effectively managed, the potential impacts and risks associated with solid wastes first need to be 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.

Whilst recognising that knowledge of the key waste properties or characteristics is an essential and integral part of quantitative environmental impact predictions, currently available data pertaining to the characteristics of solid mineral wastes is largely incomplete and inconsistent, and the mechanisms of leachate generation poorly understood (discussed in more detail in Section 1.1.2 and Chapter 6 of the thesis). It is this shortcoming that this particular study attempts to address, through the development of a generalised strategy for the prediction of key solid mineral waste characteristics, in terms of their potential environmental significance.

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 primary 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 thesis.

1.1 Background and motivation

The targeted metal in any ore deposit is present in relatively small quantities and the mineral-based resource industries 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, 2003b).

This section highlights a number of relevant issues pertaining to solid mineral wastes from the primary 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. The resultant contaminant bearing leachant is transported to the base of the bulk deposit and, unless contained, will continue to migrate into the surrounding soils and groundwaters, causing a pollution plume. 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.

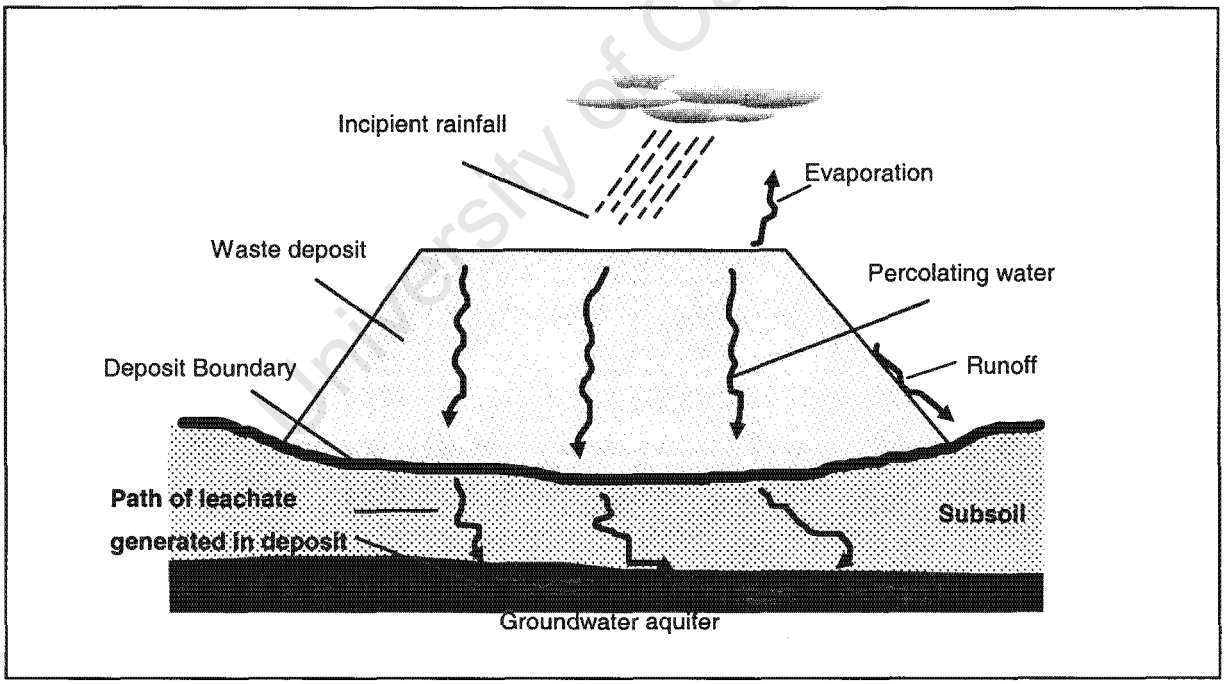


Figure 1.1: Leachate generation and transport from a solid waste disposal site.
(Hansen, 2004; Petersen, 1998)

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 mineral waste impact assessment

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 information pertaining to the environmental aspects of a product or process. Whilst the various environmental assessment tools can differentiate 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

[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.

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, leaving 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, are reported to be largely incomplete, inconsistent and very uneven (see for example discussions by 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. There is also 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.

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

Quantitative impact prediction modelling and risk characterisation

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 aid 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*".

In an effort to address these current shortcomings, Hansen (2004) developed an integrated and rigorous methodology for solid mineral waste impact assessment in the context of coal and combustion wastes. This approach views waste deposits as additional "unit operations", and leachate generation within the waste deposit is decoupled from its subsequent sub-surface transport (see Figure 1.2 for energy and metallic minerals). This puts the emissions from waste disposal on par with other process emissions such as direct gaseous and aqueous emissions, and establishes a clear link between the processes generating the waste, the management of the waste deposit and the resulting environmental impact. In this way the effect of 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.

In accordance with the approach of Hansen (2004), the time-dependent concentration profile of mobile constituents at the interface between the waste deposit and the surrounding environment is derived by means of a mechanistic leachate generation model, which incorporates generic equations to describe the complexities of hydrodynamic and oxygen transport in both saturated and unsaturated disposal regimes. Once the leachate concentration has been calculated, the fate and transport of the leached components into groundwater is assessed using industry-standard hydro-geology plume dispersion modelling software such as MODFLOW (McDonald & Harbaugh, 1988) and MT3D (Zheng, 1992). 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. This quantification of both the inherent spatial- and time-dependent 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).

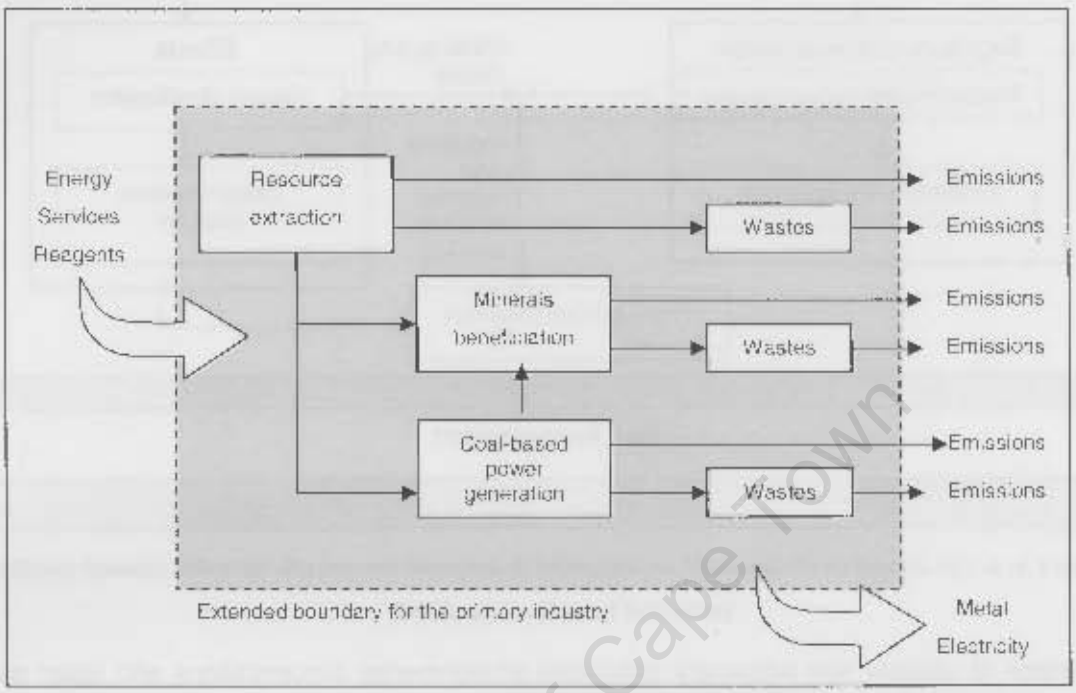


Figure 1.2: Extended process boundary for the primary industries (modified from Hansen, 2004)

The approach proposed by Hansen (2004) 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 (see Figure 1.3). 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.

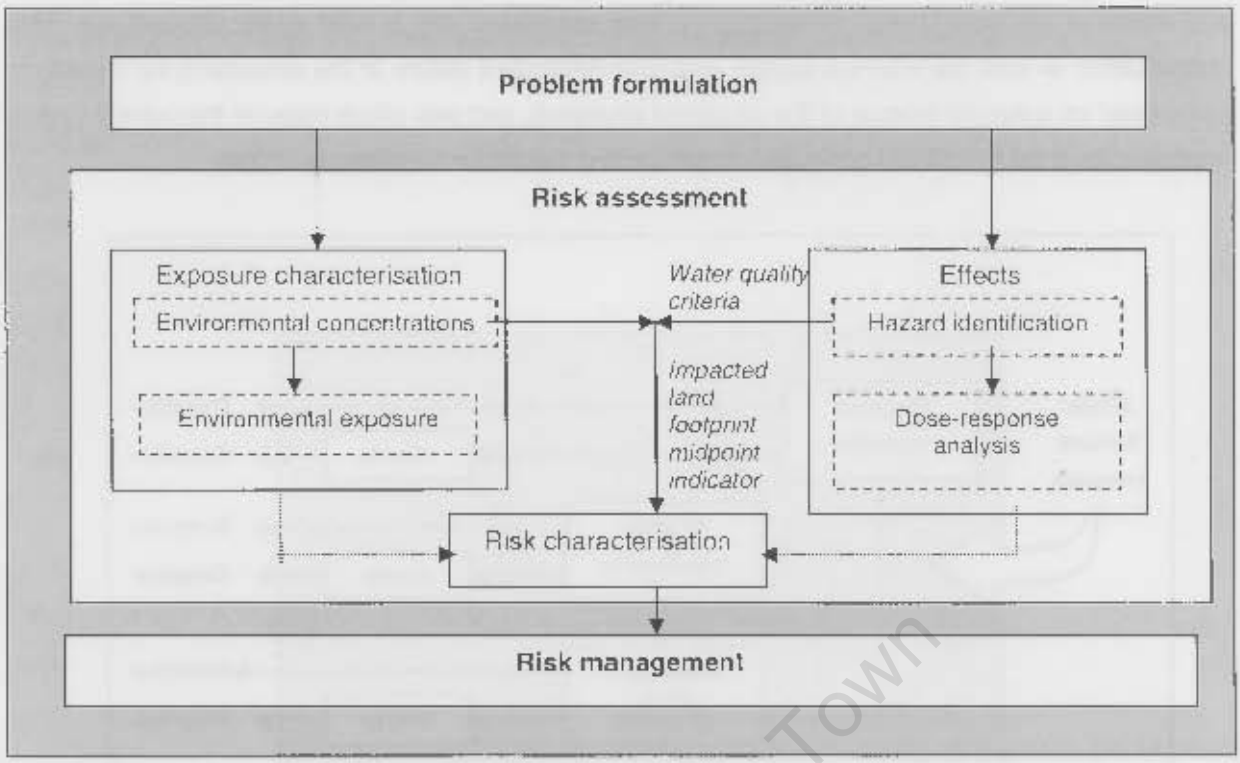


Figure 1.3: A risk-based environmental assessment procedural framework for solid mineral wastes (modified from Hansen, 2004)

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 1.4. 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.

Whilst the generic approach and leachate generation modelling capabilities developed by Hansen (2004) represent a significant advancement in terms of enabling more accurate assessment of environmental impacts from the mineral-based resource industries, application to date has been largely limited to the migration of major salts from coal wastes. Although it is recognised that an assessment of the environmental impact of solid waste disposal is not complete without a consideration of the fate of the constituent metals, the consideration of trace metal leaching will significantly increase the complexity and accuracy required by both the leachate generation and mass transport models. This is particularly the case for solid mineral wastes, which are generally composed of a multitude of trace metals in various forms; the mobility of which is controlled by a complex network of competing parameters and mechanisms.

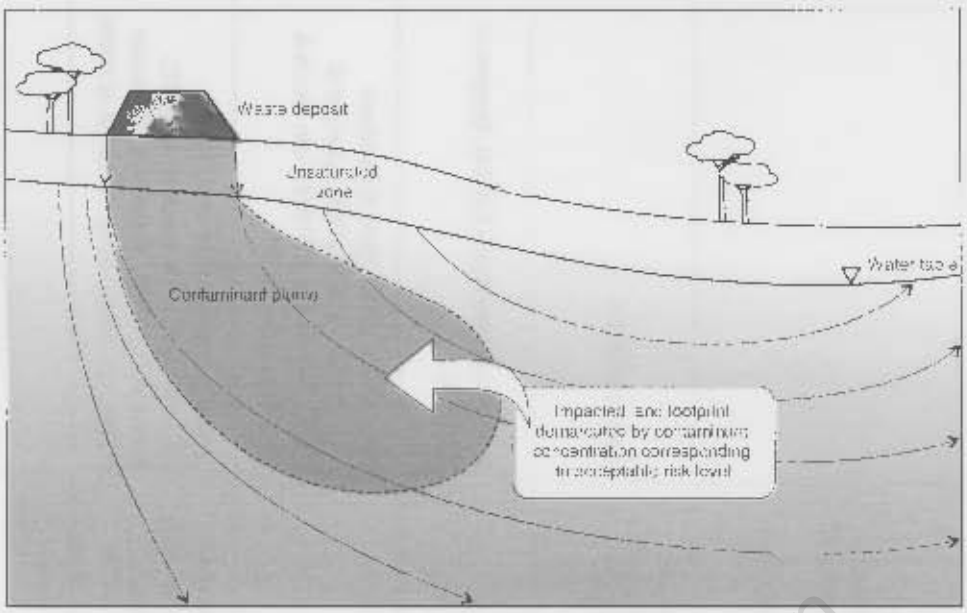


Figure1.4: Impacted land footprint showing acceptable and unacceptable regions of contamination (Hansen, 2004)

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 trace metals 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 thesis.

Solid waste characterisation for environmental impact predictions

In the broader sense, waste characterisation entails describing the qualities or properties of a particular waste material in terms of its potential environmental impact and suitability for further processing, treatment, storage or disposal.

A number of laboratory-scale methodologies have been developed for the characterisation of solid wastes, the most commonly applied ones of which are summarised in Table 1.1 overleaf.

Table 1.1: 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	Bruckard & Woodcock (2004), Butcher et al (2004)
Sequential chemical extraction tests	Quantitative information on the partitioning or distribution of trace to minor elements in major phases	Various	Dang et al (2002), Dold & Fontbote (2001), Guirco et al (2000), Leinz et al (2000), Mitchell et al (1994), van Herck & Vandecasteele (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), Strömberg & Banwart (1999), US EPA (1994), Weber et al (2004)

Table 1.1 continued.....

Test Description	Primary outcomes	Examples	Useful references
Laboratory leach tests			
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)	Eary (1990), Environment Canada (1990), Fallman & 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), Whalström (1996).
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)	

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. This can be attributed largely to the fact that 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. Furthermore, 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. Nevertheless empirical waste characterisation methods can provide useful information on the potential behaviour of solid wastes under disposal conditions, with the complexity of the leachate generation models, and consequently the reliability and accuracy of the derived results, being largely dependent on how much is known regarding the compositions of the wastes and the mechanisms governing their time-related release in a disposal scenario.

The vast number of solid waste characterisation methodologies, particularly in terms of leach tests, which differ greatly in procedural details, complexity and costs, creates difficulties in knowing when to use a particular test, or combinations thereof, and how to interpret derived results in a way that is meaningful. This situation is aggravated further by the fact that historically the main objective behind such procedures has been to classify or " type" wastes, rather than to build up a better understanding of the complex and time-dependent behaviour within waste 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 (1992), 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 mineral wastes that are poorly characterised.

As indicated in Table 1.2, each empirical waste characterisation methodology has its limitations, and is specifically designed to reveal only one or two aspects of the properties and leach behaviour of the solid under investigation. These limitations, in combination with the inherently complex nature of the solid waste disposal system, means that the derivation of information and data for impact prediction modelling will require execution of a number of different characterisation methodologies, in the form of a systematic empirical test protocol. In order to deliver results that are meaningful and reliable, the design and application of such a protocol also needs to be informed, particularly in terms of a sound fundamental 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-

dependent leach behaviour in a typical disposal scenario. It is only recently that the need for such a systematic and informed protocol of solid waste characterisation tests in terms of reliable impact prediction modelling has been recognised (Petersen et al, 2000; Sanchez et al, 2003; van der Sloot et al, 2003b; van der Sloot & Dijkstra, 2004). In the specific case of solid wastes from the primary 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 A new approach to waste characterisation- developing the hypothesis

Discussions in the previous section have provided some insights into the significance of waste characterisation in the assessment and management of solid mineral wastes, as well as the limitations and shortcomings pertaining to current availability, and empirical approaches for the derivation, of solid mineral waste characterisation data and information. This provides both the opportunity and motivation for the development of a conceptual methodological approach for predicting the key characteristics of solid mineral wastes, the development of which corresponds with the hypothesis, aims and structure of the thesis.

1.2.1 Statement of the problem

Knowledge of the characteristics of a solid waste, particularly in terms of strategic contaminants and the mechanisms and parameters controlling the leach behaviour thereof, is required in order to accurately and reliably predict the generation of leachate from, and ultimately the environmental impacts associated with, its land deposition. Unfortunately, currently available data pertaining to the characteristics of solid mineral wastes is largely incomplete and inconsistent, and the mechanisms of leachate generation poorly understood. Furthermore, 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 methodologies remain high.

The need to improve the way in which solid mineral wastes are characterised is driven not only by the limitations in terms of current data bases 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 nformation is integrated into the decision stages of a project life cycle in a time and cost effective manner.

Table 1.2: Standard 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-dependent 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 1.2 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-dependent 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-dependent 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

1.2.2 Research hypothesis and objective

The overarching aim of this research thesis is to develop a structured and generalised methodology for predicting the characteristics of solid wastes from the primary processing of mineral ore deposits, in terms of their key environmental significance.

As demonstrated in Figure 1.5, the properties or characteristics of any particular mineral waste will be directly influenced by the characteristics of the ore from which it is derived, and the process(es) from which it is generated. The selection of process(es) and/or technologies used to extract a particular targeted constituent from the ore is, in turn, largely dependent on the characteristics of the ore deposit.

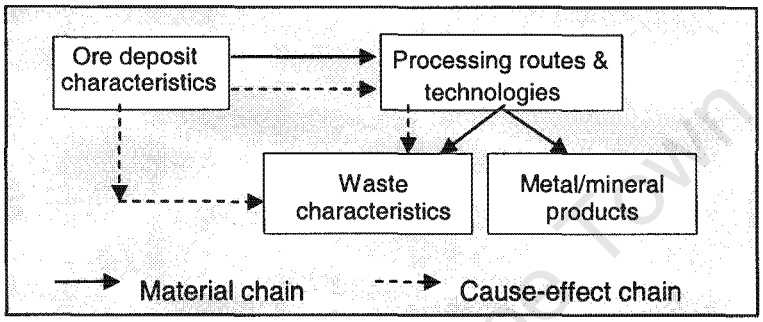


Figure 1.5: Inter-relationship between ores, processing routes and waste outputs

On this basis, the research hypothesis is formulated 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 reliable prediction of key solid mineral waste characteristics on the basis of origin and source requires detailed information and data pertaining to the compositions of ores from which they originate, as well as the deportment of such components to waste outputs during ore processing. However, as discussed in the previous section, the availability of such data and information is extremely limited, and there is currently little possibility of compiling a comprehensive, and at the same time comprehensible, inventory of process inputs and outputs for existing (let alone new) primary mineral resource operations on this basis.

1.2.3 Research approach

In line with the overarching research objective and hypothesis, a conceptual methodological approach, demonstrated diagrammatically in Figure 1.6, is proposed which essentially entails addressing current data gaps and deficiencies through reconciliation of available empirical data with a fundamental understanding of the mechanisms and parameters influencing element speciation and distribution behaviour during ore formation, extraction and beneficiation, and ultimately waste disposal. On this basis, quantitative distribution data can be generated, which, when combined with total mass flow

information, will result in a first-order inventory list of process inputs and outputs as a function of feed compositions, processing technologies, and waste management options. The hybrid semi-empirical/semi-fundamental nature of the approach is consistent with recent trends in terms of the simulation or predictive modelling of metallurgical reactors, which have been prompted largely by the recognition of the limitations associated with either purely thermodynamic modelling approaches or purely empirical approaches (Eksteen & Reuter, 2003; Georgalli et al, 2002).

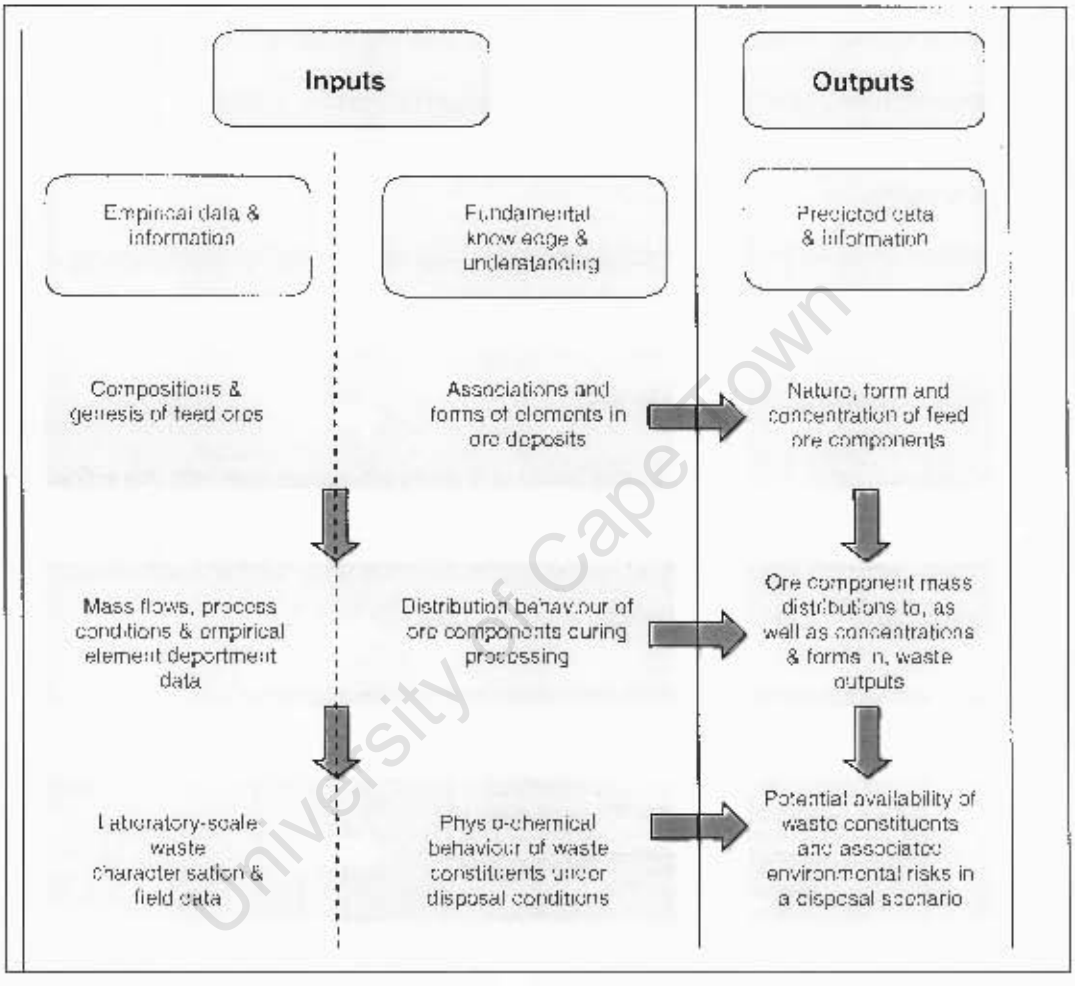


Figure 1.6: Conceptual approach for the prediction of key solid waste characteristics and associated potential environmental risk

The proposed approach for the screening of key waste characteristics on the basis of origin and source is, furthermore, underpinned by a qualitative understanding of the solid waste characteristics of key significance in terms of potential environmental risk - i.e. the link between the solid waste properties and associated environmental impacts, as well as the key factors influencing those characteristics in terms of the origins and source of the wastes- i.e. the link between feed ores, ore beneficiation processes and solid wastes. This pertains in particular to the mechanisms and parameters controlling the properties, distribution and associations of elements within ore deposits, across process unit operations and, ultimately, from solid waste disposal sites. Such an understanding forms the basis for

the establishment of generic criteria and protocols for predicting key solid mineral waste characteristics in accordance with their origins and source.

In summary this specific study aims to:

1. Develop a qualitative understanding of the key factors involved in the ore formation –› extraction & beneficiation –› waste management & disposal –› leachate generation –›environmental impact mechanistic chain, particularly in terms of reaction mechanisms and their associated parameters which influence element distributions and associations over the material transformation chain.
2. Develop generic criteria, protocols and methodological guidelines for predicting key solid mineral waste characteristics of environmental significance on the basis of their origin (ore type) and source (generating process).
3. Demonstrate the application of the proposed methodology, as well as the understanding and criteria developed in 1 and 2, by means of suitable case studies.

1.2.4 Research scope and significance

In line with the research aims, the scope of this study is specifically concerned with the influence of ore characteristics and beneficiation variables on the physio-chemical properties and leach behaviour of the solid waste outputs, and the implications of these characteristics on potential leachate concentration profiles and environmental impacts in a disposal scenario (see Figure 1.7).

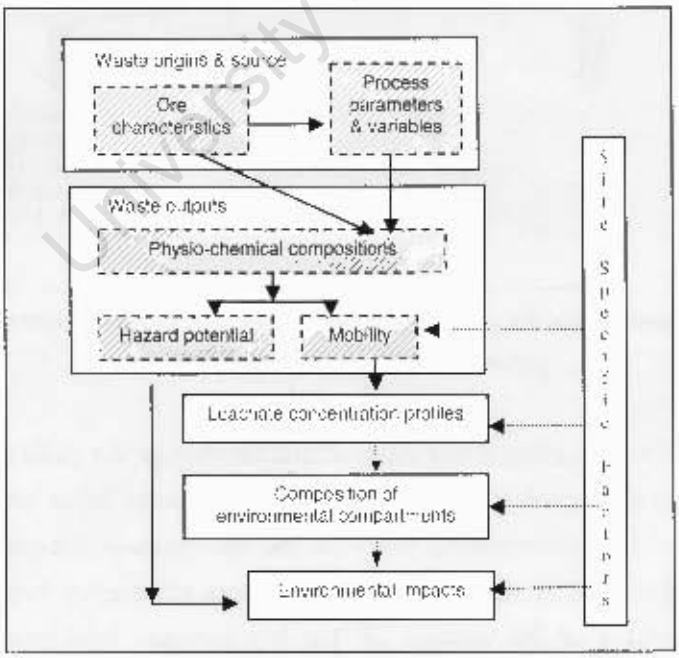


Figure 1.7: Contextualisation of the scope of study (illustrated by shaded areas and solid lines)

The accurate prediction of environmental impacts clearly requires consideration of the fate of contaminants in the subsurface environment, as well as the effects of site-specific factors (e.g.

geohydrology, local biodiversity, rainfall, disposal practices). In this work, however, the focus is specifically on waste-specific factors, and leachate generation is decoupled from its subsequent sub-surface transport, such that the environmental performance of a waste deposit is related directly to the nature of the material consigned therein, and the key factors determining such (i.e. waste origins and source).

It is furthermore postulated that the structured prediction of solid waste characteristics on the basis of origin and source will allow for more reliable and effective empirical characterisation protocols. This in turn will ensure a more accurate assessment of the time-dependent leachate generation behaviour of waste materials, ultimately resulting in more realistic quantitative impact predictions. As indicated in the previous section, the availability of prior information pertaining to the physio-chemical composition, as well as the kinetic and metabolic behaviour, of constituent components is of particular importance in terms of the intelligent design and application of an empirical waste characterisation test protocol. Apart from guiding detailed empirical and predictive modelling studies, predicted waste characterisation data can also be used, in conjunction with relatively simple mass transport equations, to conduct first-order or screening assessments of potential environmental impacts directly. A proposed systematic and iterative procedural framework for the risk-based assessment of environmental impacts, in which the preliminary screening of waste characteristics on the basis of origin and source is a fundamental component, is presented in Figure 1.8.

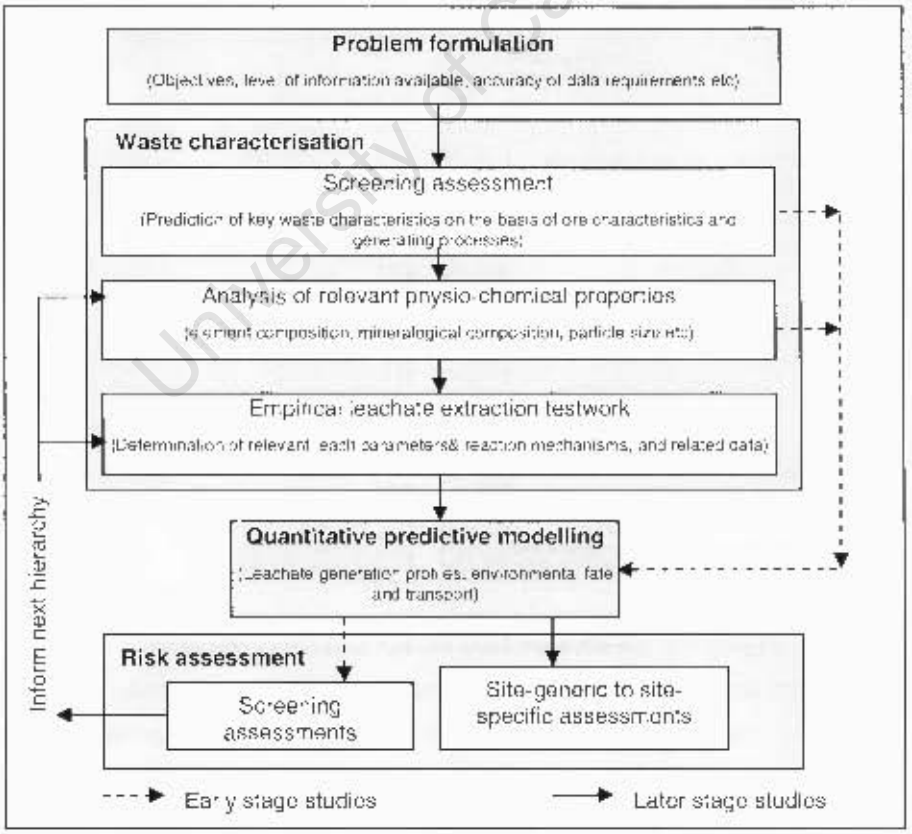


Figure 1.8: Procedural framework for the systematic assessment of environmental risks associated with solid mineral wastes

The prediction of waste characteristics on the basis of origin and source can clearly play a key role in informing decision-making in the early stages of a project life-cycle, as well as in guiding further data collection and performance assessment studies in later project stages. Whilst the focus of this particular study is specifically on environmental performance, a better understanding of the distributions of minor and trace ore components during beneficiation can also play an important role in the evaluation of other performance criteria, including economic viability and, in particular, eco-efficiency[2].

Of key importance in terms of the accuracy and specificity of predicted waste characterisation data and information, is the iterative or hierarchical nature of typical process design and data collection protocols. As demonstrated diagrammatically in Figure 1.9, the selection of process options to deliver designs consistent with internationally accepted sustainability principles is ideally conducted in an iterative manner, with increasing articulation of detail and reduced uncertainty as one progresses from the conceptual to the final design stages.

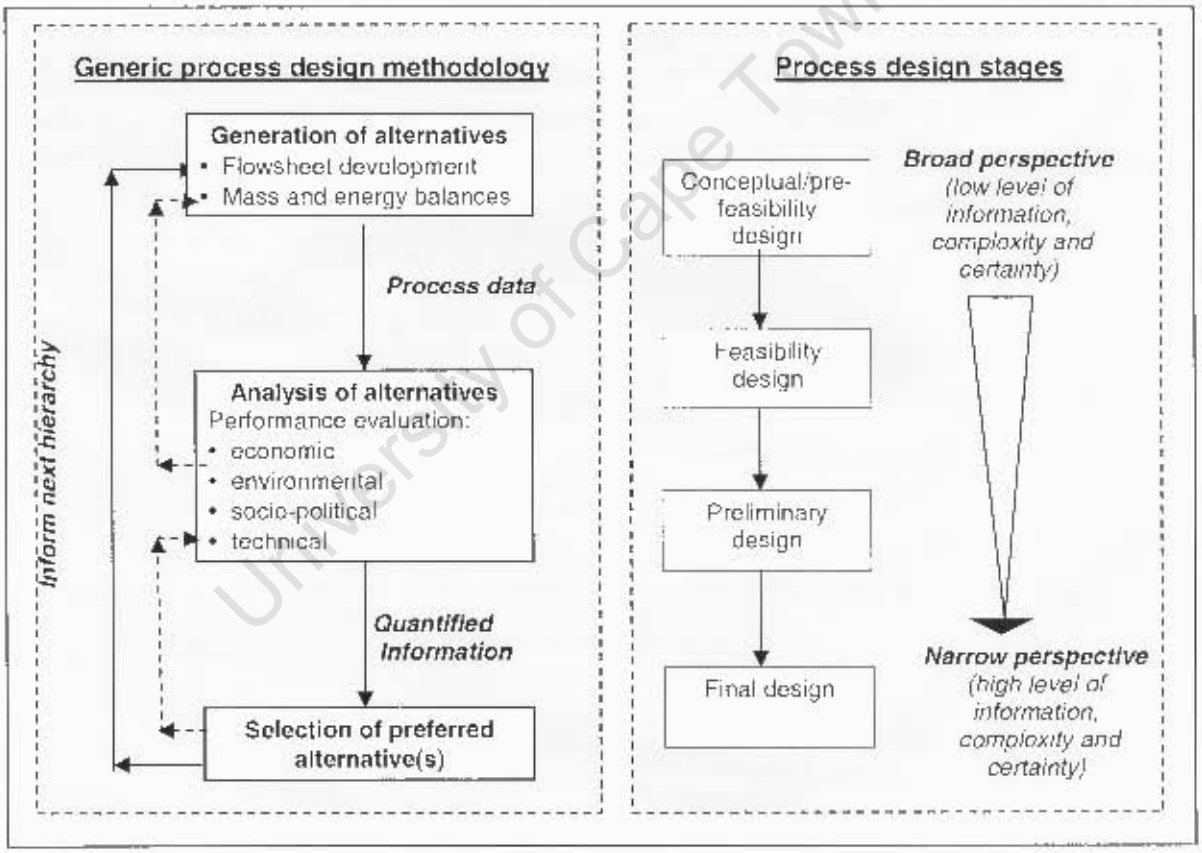


Figure 1.9: Iterative process design and data collection

This systematic approach ensures that data and information requirements remain manageable and that processes are designed and implemented in a cost and time efficient manner. This is particularly

[2] Eco-efficiency has been identified by the World Business Council for Sustainable Development (WBCSD, 1996) as a key driver for companies in terms of meeting sustainability objectives – combining economic improvements with more efficient use of resources and the prevention of environmental emissions or degradation.

important in the early design stages which are usually characterised by a large number of alternatives (typically 7-15) and relatively broad system boundaries (see discussions by Basson & Petrie, 2003; Stewart et al, 2003a).

The generic approach outlined in the previous section is thus aimed at generating characterisation data which is in line with early design stage or screening risk assessment information requirements in terms of uncertainty, a reasonable degree of which is both necessary and desirable. In accordance with Douglas (1998), such uncertainty is typically in the range of 25% to 40%, and is indicative of typical or generic, rather than absolute, values.

1.3 Thesis structure and layout

The approach to fulfilling the aims and scope of this study, as outlined in the previous sub-section, is closely reflected in the thesis layout, as represented schematically in Figure 1.10.

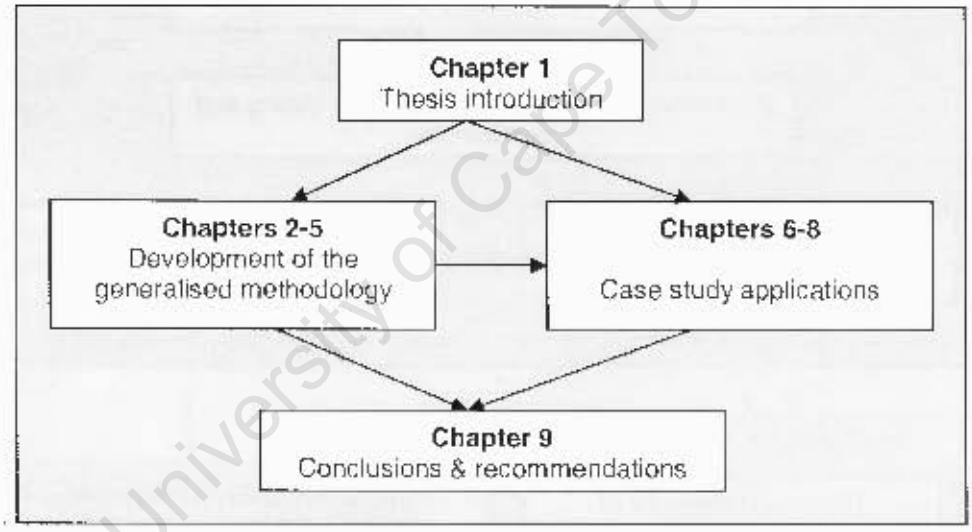


Figure 1.10: Schematic representation of the thesis structure

Chapters 2 to 5 are aimed at developing the qualitative understanding, protocols and methodological guidelines which underpin the proposed predictive approach, thereby fulfilling the first two key research objectives. Specifically Chapter 2 identifies solid waste characteristics of key significance in terms of their potential environmental impact and risk, thus establishing the framework for the exploration of those factors that contribute to variations in identified characteristics, as a function of ore type and characteristics (Chapter 3), and subsequent processing routes and reactor technologies (Chapter 4). General methodological guidelines in terms of the technical tasks associated with the predictive approach are outlined in Chapter 5.

In line with the third specific research objective, application of the approach is demonstrated by means of appropriate case studies in Chapters 6 to 8. The primary copper production industry sector has been selected for this purpose, as it is a well-defined and described industry that encompasses many of the

complexities and problems typically associated with the primary mineral-based resource industries. These relate in particular to the presence of multiple co-elements, complex process flow-sheets, as well as large volume wastes posing a relatively high environmental risk. Three separate but inter-related case studies, as presented in Figure 1.11, have been selected to specifically demonstrate the key features of the generic rule-based methodology developed in the preceding chapters of the thesis. Such features pertain in particular to predictions of the chemical and mineralogical compositions of ore deposits (case study 1), the subsequent distribution of ore components during ore beneficiation (case studies 1 and 3), and the resulting environmental implications associated with the land disposal of solid waste outputs (case study 2).

Finally, Chapter 9 discusses the significant findings and conclusions, and proposes a way forward.

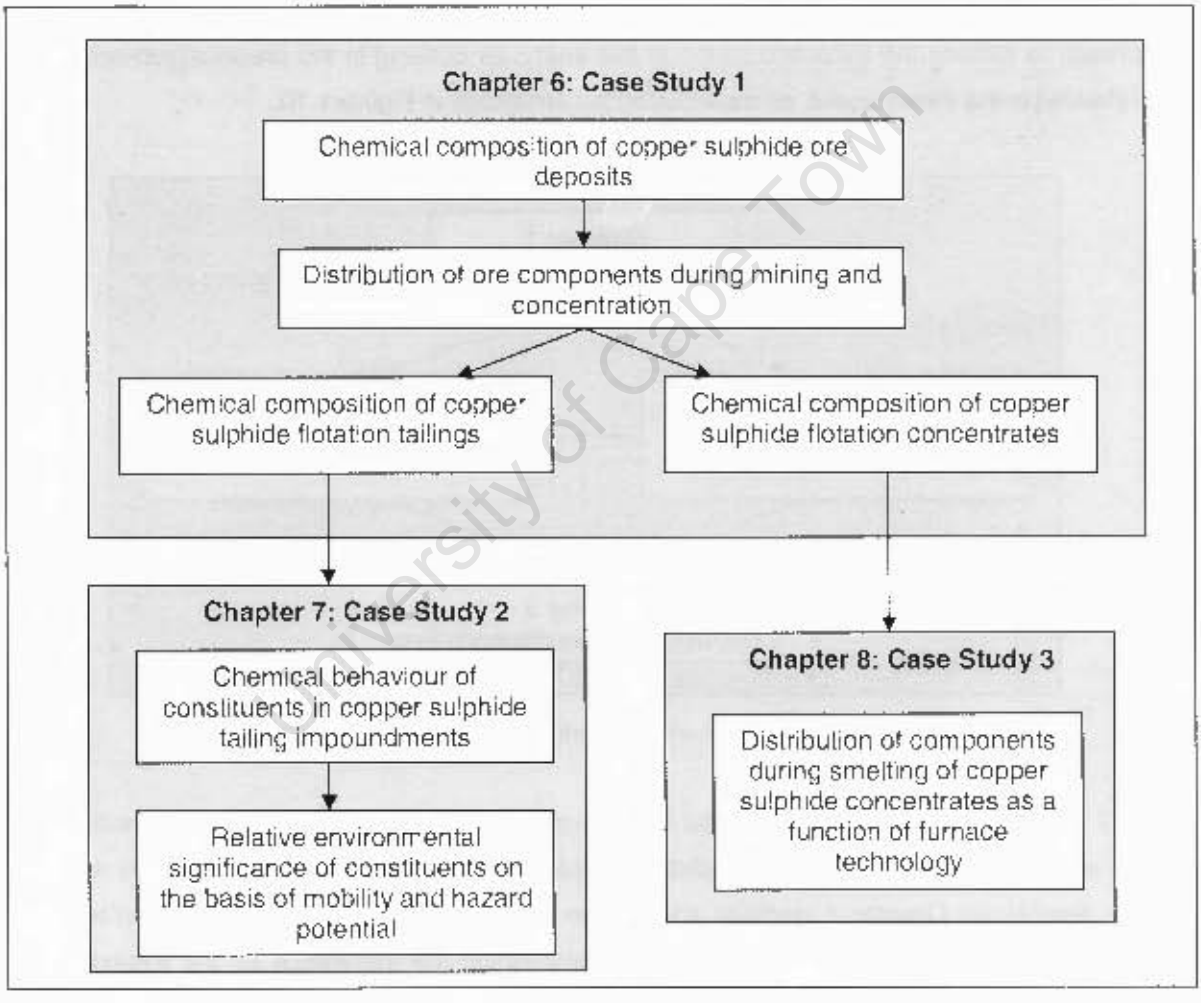


Figure 1.11: Lay-out of the case study applications

2

Solid Mineral Waste Characteristics: Establishing the Link between Waste, Leachate and Environmental Impact

A qualitative understanding of the solid waste characteristics of key significance in terms of potential environmental impact and risk predictions is an integral and essential part of the proposed methodology for the prediction of key solid mineral waste characteristics. Based on this understanding environmental impacts can be related back through the waste → leachate → (environmental concentration) → environmental impact chain to the characteristics of the leachate generated by a waste disposal site and ultimately to the characteristics of the waste material contained therein.

A review of the open literature (e.g. Bourg, 1995; Eary et al 1990; ICMM, 1995; Jones, 1995; OECD, 1993; Parametrix, 1995) indicates that there are three over-arching criteria which need to be met in order for a solid mineral waste to pose a risk to the environment, viz.

1. One or more of the components must have an inherent capacity or potential to cause harm; *and*
2. The hazardous component(s) must be present in the waste in environmentally significant concentrations or quantities; *and*
3. The hazardous component(s) must be available for uptake or adsorption by organisms i.e. they must be bioavailable. In order to be bioavailable, solid waste components first need to be available for release from the disposal site, and subsequently transported within the environment i.e. such components need to be environmentally available in order to be bioavailable. If a solid waste component is immobile under specific disposal conditions, it will not be environmentally available and will thus pose no environmental risk, regardless of its hazard potential and concentration within the solid waste.

Both the hazardous nature and the mobility of solid waste constituents are, in turn, dependent to a large extent on the constituent concentration.

As illustrated in Figure 2.1, the potential environmental risk posed by a solid waste can thus be considered a function of two main criteria, viz. the hazard potential of the waste constituents and the possibility of such constituents becoming mobile or available for release to the environment under disposal conditions.

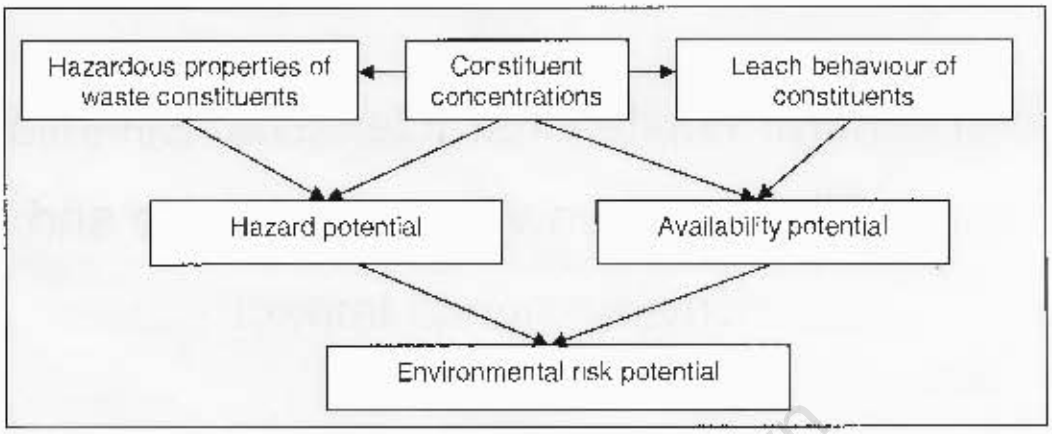


Figure 2.1: Solid waste properties of key environmental significance

The key factors influencing the hazardous properties and availability of typical solid waste constituents are identified and assessed in Sections 2.1 and 2.2 respectively. This knowledge will form the basis for subsequent comparisons of ore (Chapter 3) and processing (Chapter 4) factors which contribute to variations in these characteristics. The criteria for evaluating the hazard and availability potential of solid waste constituents can furthermore be applied to estimate and compare the relative environmental risk associated with each of the various constituents, in accordance with the generic protocol proposed in Section 2.3.

2.1 The hazard potential of typical solid mineral waste constituents

The identification of the hazards associated with a particular chemical species is commonly used to type or classify substances according to their hazardous properties and associated risks (e.g. acutely toxic, moderately toxic, corrosive, flammable etc), and is an important part of conventional environmental risk assessment (ERA) procedures (as illustrated diagrammatically in Figure 1.3, Section 1.1).

This sub-section identifies specific hazard potential criteria of key environmental significance in the case of solid wastes from the primary mineral-based resource industries (Section 2.1.1), and uses these criteria to group and rank typical solid waste constituents accordingly (Section 2.1.2).

2.1.1 Identification of key hazard potential criteria for solid mineral wastes

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. Subsequent migration of contaminants within the surrounding environment can lead to ecotoxic and human toxic effects, and may also have an adverse effect 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).

Contamination of natural resources does not necessarily result in pollution or constitute an environmental impact. Vegter (2001) defines contaminants as substances found in a medium at a concentration higher than expected from other considerations, and where the source of the additional concentration of the substance is as a direct result of human activity. Furthermore, a contaminant is only considered a pollutant if the observed contamination is high enough to cause harm or damage. The release of a substance to the environment must thus occur at a concentration which is both elevated in comparison to "naturally occurring background levels" and high enough to cause some form of harm or damage, in order to have an adverse environmental effect.

The relationship between concentration and toxicity is particularly important in the case of naturally occurring elements, which comprise the bulk components in solid waste from the primary mineral-based resource industries. Whilst many of these naturally occurring elements exhibit toxic properties at high doses, certain elements are essential for life and are required in mammalian and plant nutrition. The biological significance of naturally occurring elements in terms of essentiality is summarised in Table 2.1. It should, however, be noted that the concept of essentiality is under constant review as research makes progress, and an unequivocal classification is virtually impossible.

Table 2.1: Essentiality of naturally occurring elements (ANZECC, 1999; Cox, 1995; Fŏrstner & Wittman, 1981; Logan & Traina, 1993; Torrey, 1978)

Non-essential	Essential	
	Humans and animals	Plants
Al ,Sb, Be, Cd, Pb, Bi, Hg, Ag, Pb, Li, Br, Rb, Sr, Cs, Sr, Sc, Ti, Zr, Hf, Ta, Nb, Re, PGMs, Au, In, Tl, Br, Te	***Micro-nutrients:*** Cr, Cu, Fe, Mn, Mo, Ni, Se, (Sn) , F, I, Co, Zn, (V), (Si), (As), (B), (W), (Ba) ***Macro-nutrients:*** Na, Ca, S, P, Mg, K, Cl	***Micro-nutrients:*** B, Cu, Fe, Mn, Mo, Zn, V, (Ni), Cl ***Macro-nutrients:*** Mg, K, P, Ca, S
Note: Figures in brackets represent possible nutrients.		

As indicated by the dose-response curves in Figure 2.2 below, both deficiencies and excesses of essential elements can adversely affect the health of an organism. In contrast, non-essential elements have a negligible effect on organisms at a below-threshold level, becoming increasingly toxic as the dose increases above this level.

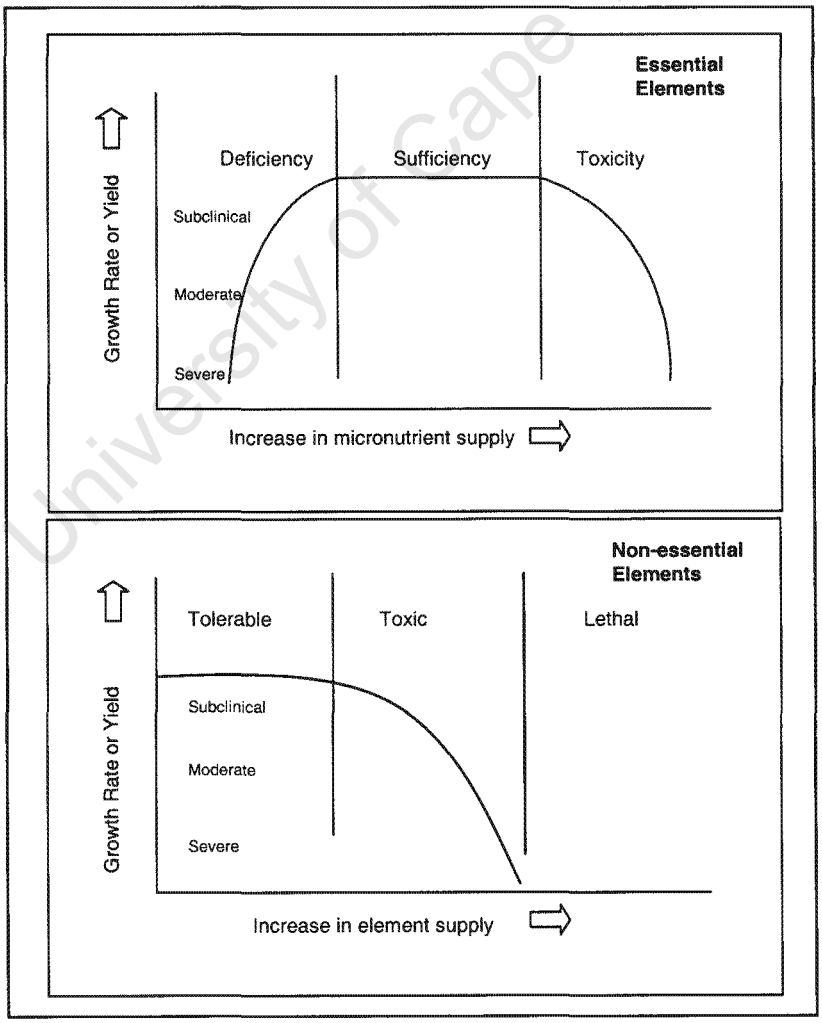


Figure 2.2: Typical dose-response diagram for essential and non-essential elements (Fŏrstner & Wittman, 1981)

Whilst virtually all elements are toxic when supplied in excess of optimum (essential) or tolerable (non-essential) levels, the concentrations at which toxicity and/or deficiency occurs will vary quite considerably for the different elements. Highly toxic elements will exhibit toxicity at relatively low concentrations, whilst elements exhibiting a "low" or "moderate" toxicity will exhibit toxic effects at considerably higher levels.

Toxicity, or the level at which toxic effects occur, is, however, also dependent on a number of other factors (see for example reviews by ANZECC, 1999; Chapman & Wang, 2000; Dallas & Day, 1993; Förstner & Wittman, 1981; Logan & Traina, 1993; Parametrix, 1995; Rubenstein & Segal, 1993). Whilst chemical form or speciation is of particular relevance to metal and metalloids (see Table 2.2), toxic effects of trace metals will also be highly dependent on the nature and life history of the exposed organisms (including aspects such as age, sex, levels of starvation and activity). An evaluation of the toxicity of metals and metalloids is further complicated by the ability of organisms to genetically adapt to changes in metal concentration levels, and by the synergistic or antagonistic effects of metals occurring simultaneously.

Table 2.2: The environmental significance of chemical forms (Logan & Traina, 1993)

Element	Dominant aquoous chemical form	Most toxic chemical form
Ag	Ag^{+}	Ag^{-}
As	AsO_4^{3-} ; AsO_3^{3-}	AsO_3^{3-}
B	$B(OH)_3$	$B(OH)_3$
Ba	Ba^{2+}	Ba^{2+}
Be	Be^{2+}	Be^{2+}
Bi	Bi^{3+}	Unknown
Cd	Cd^{2+}	Cd^{2-}
Co	Co^{2+}	Co^{2+}
Cr	Cr^{3+}; CrO_4^{2-}	Cr^{6+}
Cu	Cu^{2+}	Cu^{2+}
Hg	$Hg(OH)_2$, $HgCl_2$	CH_3Hg
Mn	Mn^{2+}	Mn^{2+}
Mo	MoO_4^{2-}	MoO_4^{2-}
Ni	Ni^{2+}	Ni^{2+}
Pb	$Pb(OH)^{+}$	Pb^{2+}
Sb	$Sb(OH)_6^{-}$	Unknown
Se	SeO_4^{2-}	SeO_4^{2-}
Zn	Zn^{2+}	Zn^{2+}

In short, the characterisation of toxicity in terms of damage to humans, wildlife and plants on the basis of exposure-effect modelling is difficult, and fraught with uncertainty and inconsistency. In many cases reliable data pertaining to toxicological properties of substances are not available, particularly in the case of trace metals, and the cause-effect chains not clearly understood.

Water quality guidelines, such as those developed by the South African Department of Water Affairs and Forestry (DWAF,1996) and the Australia and New Zealand Environment and Conservation Council (ANZECC,1999) provide both a convenient and sufficiently accurate measure of the degree of potential harm or damage that a contaminant has the potential to cause if released to the environment. Such guidelines have been developed to ensure protection of the environment, using available toxicological data and risk-based statistical methodologies. Furthermore they have the added advantage of being linked to end usage of water (human consumption, crop irrigation, livestock watering, protection of aquatic ecosystems and recreation), and take into account toxicity as well as aesthetic and physical effects.

Table 2.3 groups and ranks naturally occurring elements in accordance with the water quality guidelines developed by DWAF (1996) and ANZECC (1999) i.e. guidelines taking into account toxic, aesthetic and physical effects of contaminants on usability of water. Detailed water quality guidelines are presented in Appendix 2.1.

Table 2.3: Toxic and aesthetic effects on the basis of water quality guidelines

Group	Domestic consumption	Agricultural use		Aquatic ecosystems
		Animal watering	Crop irrigation	
Group I: Elements having a severe effect	Hg, Cd, Sb, As, Pb, Se	Hg, Cd, Se, Pb	Hg, Cd, Mo, U	Ag, Cd, Hg
Group II: Elements having a high-moderate effect	***Toxicity:*** Ni, Cr, CN, Cu, F, B, Ba, V ***Aesthetics:*** Al, Mn, Fe, Zn	U, As, Cr, Ni, Co, F, Al, B, Fe, Mn, Zn, Cu	***Toxicity:*** Se, Cu, As, Be, Cr, Cu, Ni, B, F, Zn, Pb, Ba, F, Li ***Equipment fouling:*** Fe, Mn	Co, Cu, Ni, CN, Cr(VI),Al, Pb, Se, As, Zn, U, B, V, Mo, Fe, Se
Group III Elements having a low-moderate effect	***Toxicity:*** NO_3, SO_4 ***Aesthetics:*** Na, Cl, Ca	Mg, Ca, Na, Cl, SO_4		Mg, NO_3, Mn

Quantitative Water Quality Guidelines:

Group I: Human consumption: <0.01 ppm; livestock watering: <0.1 ppm; crop irrigation: <0.01 ppm; aquatic ecosystems: <0.1 ppb

Group II: Human consumption: 0.01-3 ppm; livestock watering: 0.2-20ppm; crop irrigation: 0.02-5 ppm; aquatic ecosystems: 0.2-10ppb

Group III: Human consumption: 30-500ppm; livestock watering: 100-2000ppm; crop irrigation: 40-300 ppm; aquatic ecosystems: 20-200ppb

No quantitative guidelines available for Ti, Zr, Hf, Nb, Re, W, Ge, Ga, Bi, Tl, Sn, In, Te.

As noted, there are a number of elements for which water quality guidelines are not currently available. This is due to the fact that current toxicological data is not available or not considered sufficiently reliable. Guidelines for aquatic ecosystem protection are often the most stringent, and generally ensure that other related environmental values, such as edible fish and shellfish, are also protected.

It is, however, recognised by authorities (DWAF, 1996; ANZECC, 1999) that the nature and level of risk associated with solid waste leachate generation and transport will be highly site-specific. Water quality guidelines should thus be perceived as "trigger" rather than blanket levels, and will need to be adapted in accordance with local or site-specific conditions, such as local organisms or ecosystems, background levels and other hydrogeological or climatology factors which may modify toxicity or bioavailability. Site-specific back-ground levels, in particular, have important implications in terms of the biological significance of contaminants, as all organisms are dependent on essential metals for optimum growth and development and are thus acclimated to a range of bioavailable metal background concentrations occurring in their natural habitat. The typical effect of background concentration levels on the deficiency-toxicity curve is illustrated in Figure 2.3.

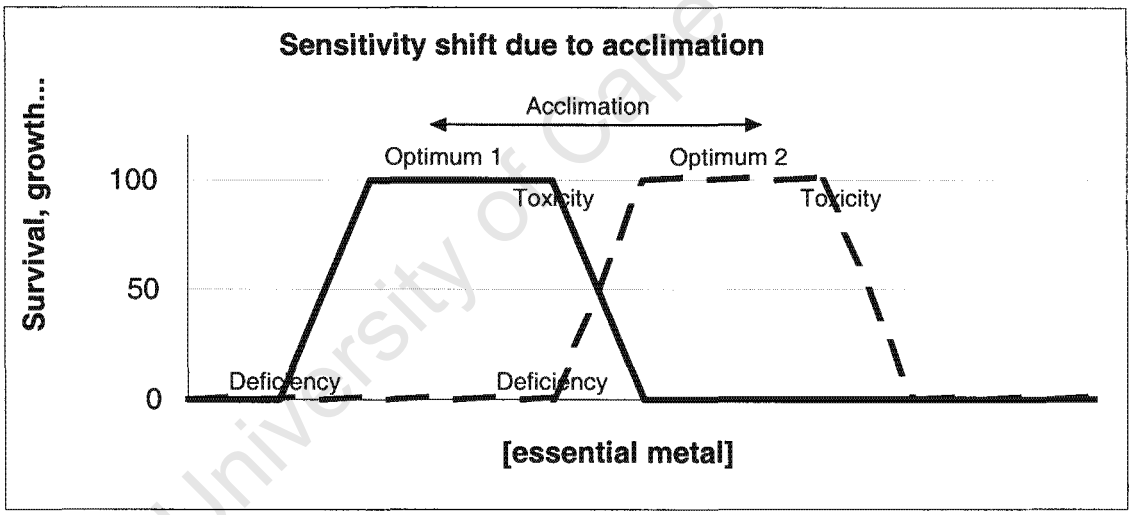


Figure 2.3: Effect of background concentrations on the deficiency-toxicity curve (Chapman & Wang, 2000)

Whilst back-ground concentrations can vary quite considerably for different sites and regions, a generic indication of typical concentrations in natural soils, surface waters and within the earth's crust provides a first-order indication of the relative abundance of elements in natural environments, and typical concentration ranges that might be expected.

Table 2.4 groups and ranks elements according to their relative abundance in natural environments, on the basis of typical concentration levels within the earth's crust, uncontaminated soils and freshwaters (ANZECC, 1999; Beus & Grigorian, 1977; Chapman & Wang, 2000; Cotton & Wilkinson, 1962; Cox, 1995; Logan & Traina, 1993; Tadessa et al, 1994; US EPA, 1995). Typical environmental concentrations are presented in Appendix 2.2.

Table 2.4: The abundance of elements in natural environments

Group	Crust & soils	Freshwaters
Group I Scarce elements	Ge, Sb, In, Hg, Ag, Tl, I, Cd, Bi, Se, Au, Re, Te, PGMs	Tl, Cd, Hg, Mn, Co, Cr
Group II Trace elements	Zr, REE, Ni, Zn, Cu, Li, Sn, Co, Pb, Nb, Ga, W, B, Mo, U, Ta, Cs, Be, As, Br, Hf, Sc	Ni, Se, U, V, I, Sb, As, Cu, Pb, Zn
Group III Minor elements	Mn, F, S, Cl, Ba, Rb, Cr, V, Ti, P	F, K, Mg, Fe, Si, S, Na
Group IV Major elements	Si, Al, Fe, Ca, Na, K, Mg	

Group I: Crust & soils: <1ppm; freshwaters: <1ppb
Group II: Crust & soils: 1<ppm<100; freshwaters: 1-10ppb
Group III: Crust & soils: 0.1-1%; freshwaters: 1-10ppm
Group IV: Crust & soils: 2-28%

2.1.2 Ranking and grouping of solid waste constituents in accordance with key hazard potential criteria

On the basis of the discussion in the previous section (2.1.1), criteria considered to be of key significance in terms of evaluating and prioritising the hazard potential of typical solid mineral waste components include:

- biological relevance in terms of both toxicity and essentiality
- aesthetic (taste, odour, colour) and physical (corrosion, fouling) properties
- natural background levels.

Table 2.5 groups and ranks constituent contaminants commonly associated with solid mineral wastes in accordance with the above-mentioned criteria.

Table 2.5: Generic ranking and grouping of typical solid mineral waste components on the basis of hazard potential

Components	Common hazard characteristics	Measurable indicators
Major soluble salts Na, K, Mg, Ca, sulphate, chloride, bicarbonate, nitrate	All essential macro-nutrients, low-moderate toxicity (only toxic at relatively high concentrations), relatively abundant (minor-major) in natural environments.	TDS or EC
Trace-minor soluble constituents (Metals, metalloids, minor salts)		Individual concentrations
Group A: High-severe hazard potential		
1: Cd, Hg	1.Toxic to all organisms at low concentrations; non-essential & relatively scarce in natural environments	
2: Sb, Pb, As, Se, Ag, Tl, Te, In, Cr(VI), CN	2. Relatively high toxicity, partial to non-essential, scarce in natural environments	
3: Bi, Re, Ge	3. Toxicity uncertain (generally moderate), non-essential, scarce in natural environments	
Group B: Moderate-high hazard potential		
1: Ni, Cr (III), Cu, Co, B, U, Zn, Be, Mo	1: Mainly essential at low concentrations, toxic at higher concentrations, present in trace quantities in natural environments	
2: Mn, Fe, Al, Ba, V, F	2: Majority micronutrients, toxic or aesthetic effects at elevated concentrations, relatively abundant	
3: Sn, Br, Ga, W, Li, Zr, Ta, Hf, Sc, I, REE	3: Toxicity uncertain (generally low-moderate), predominantly non-essential and present as trace elements	
Group C: Low - moderate hazard potential		
Ti, P, Rb	Essentially low toxicity and relatively abundant.	
Acidity H+, OH-	Negligible direct toxic effects over quite a wide range (pH 5.5-8).	pH

On the basis of properties of potential environmental concern, the typical constituents of a solid mineral waste can be divided into three generic groups, viz: major soluble salts; trace-minor soluble metals, metalloids and soluble salts; and acidity.

- ***Major soluble salts:*** The soluble salts (sulphates, chlorides, bicarbonates and, to a lesser extent, nitrates and phosphates) of calcium, magnesium, sodium and potassium are relatively common in uncontaminated soils and water, due to both their abundance in the earth's crust as well as their relatively high solubilities. Soluble salts are normally expressed in terms of salinity, using either TDS (Total Dissolved Salts) or EC (Electrical Conductivity) as quantitative measures.

  The major soluble salts are essential macro-nutrients to all living organisms and, in the case of mammals and plants, only exhibit toxic effects at relatively high concentrations. In terms of water quality for human consumption, guidelines are mainly based on aesthetic and physical properties (taste, scaling and corrosion), rather than toxicity. Most aquatic organisms can only adapt to a narrow range of salinities, above or below which direct toxicity occurs as a result of physiology changes. Freshwater ecosystems are particularly sensitive to *increases* in salinity.

  Salt accumulation or salinisation is also a major source of concern in terms of the degradation of agricultural land. Sodicity, a measure of the proportion of Na relative to other cations in soil, is a condition that degrades soil properties by making soil more dispersible and erodible, restricting water entry and reducing hydraulic conductivity. These factors result in salt accumulation and make the soil more susceptible to erosion. Sodicity is frequently used as a measure or indicator of soil structural stability.

  Salinisation in terms of degradation of soil and water resources, and consequently on the future availability for their use, has been highlighted as a major concern in water-scarce countries such as South Africa and Australia.

- ***Trace-minor soluble constituents:*** This group includes metals, metalloids (or semi-metals), as well as minor inorganic soluble salts such as cyanide, fluoride and, to a lesser extent, bromide and iodide, which are frequently used as reagents in the processing of ore deposits.

  Unlike the major soluble salt-forming elements outlined above, these elements can vary quite considerably in terms of both their biological effect and environmental concentrations. Whilst many of the elements (particularly Si, Al, Fe, and to a lesser extent Mn, Ba, Rb, Cr, V, Ti) in this group are present in soils and the earth's crust in significant quantities, they generally do not occur within natural (uncontaminated environments) in significant quantities in soluble or bioavailable form (in freshwater) and are only essential, if at all, in minor quantities (i.e. as micro-nutrients).

- ***Acidity:*** Acidity is normally expressed in terms of the free hydronium ions (H^+ or H_3O^+) and measured in terms of pH (-log H^+ concentration).

  Most species are tolerant to a relatively wide range of environmental pH values, and will remain unaffected in the range 5.5-8. Low pH values (<5.5) can, however, have a direct toxic effect on a

number of aquatic insects and fish. In terms of human consumption and agricultural use, water quality guidelines are mainly based on corrosion and scaling problems.

The main effect of pH is indirect, with pH having a major influence on the solubility and hence bioavailability of metals and metalloids. In accordance with authors such as Jones (1995), pH is considered to be the master variable controlling the leachability of metal species from solid mineral wastes. The influence of pH on element mobility is discussed further in the following section.

2.2 The mobility of typical solid mineral waste constituents

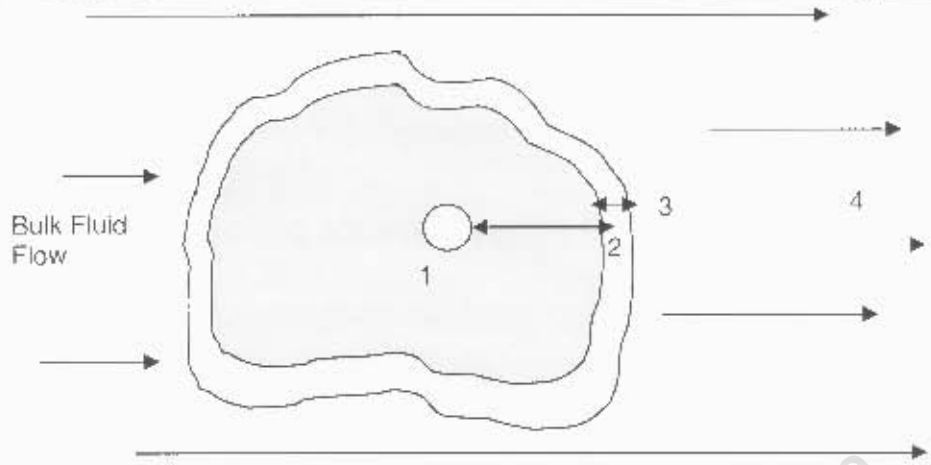
As previously discussed, in order to pose an environmental risk, waste constituents need to have both an inherent capacity to cause harm or damage, and be available for release to the surrounding environment i.e. risk is a direct function of the constituent's hazard potential and availability for release (mobility) from the waste deposit.

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 2.4. The rate and extent of leaching, and the governing mechanisms, will, furthermore, be dependent 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 line with the research aims, this section is concerned mainly with those characteristics or properties of a solid mineral waste which have a key influence on the chemical mobility of constituents considered to be of potential environmental significance, including major soluble salts, trace-minor soluble constituents and acidity. In order to develop an understanding of such a system, it is important to first gain an appreciation of the complexities involved and the processes occurring within the said system. To this end, Section 2.2.1 reviews the various chemical processes and parameters influencing the mobility of metals and salts in inorganic[3] solid waste

[3] Organic contaminants and processes involving organics are specifically excluded as these are not considered to be significant components of solid wastes from the primary resource-based industries.

deposits. Based on this understanding, Section 2.2.2 discusses the interaction and overall effect of the key processes and parameters on the chemical behaviour of solid wastes specific to the primary metal production and coal-based power generation industries.



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

2.2.1 Inorganic solid waste reaction mechanisms

In accordance with the general literature (see for example Bourg, 1995; Eary et al, 1990; ICMM, 1995; Jones, 1995; OECD, 1993; Paramotrix, 1995), the main reaction mechanisms controlling the mobility of typical solid waste constituents include dissolution/precipitation, oxidation/reduction and adsorption/desorption reactions.

Precipitation and dissolution are arguably the most important reactions in terms of their control on the compositions of salts and metals[1]. In many cases the release of contaminants and weathering of inorganic solid waste deposits can be largely considered within the framework of relative solubilities of the constituent compounds. These solubilities can be inferred from a consideration of the stable forms of the elements under atmospheric conditions, which are, in turn, a function of ionic radii and charge densities (see Figure 2.5).

[1] For the purposes of this study, the term "metals" is assumed to include metalloids or semi-metals.

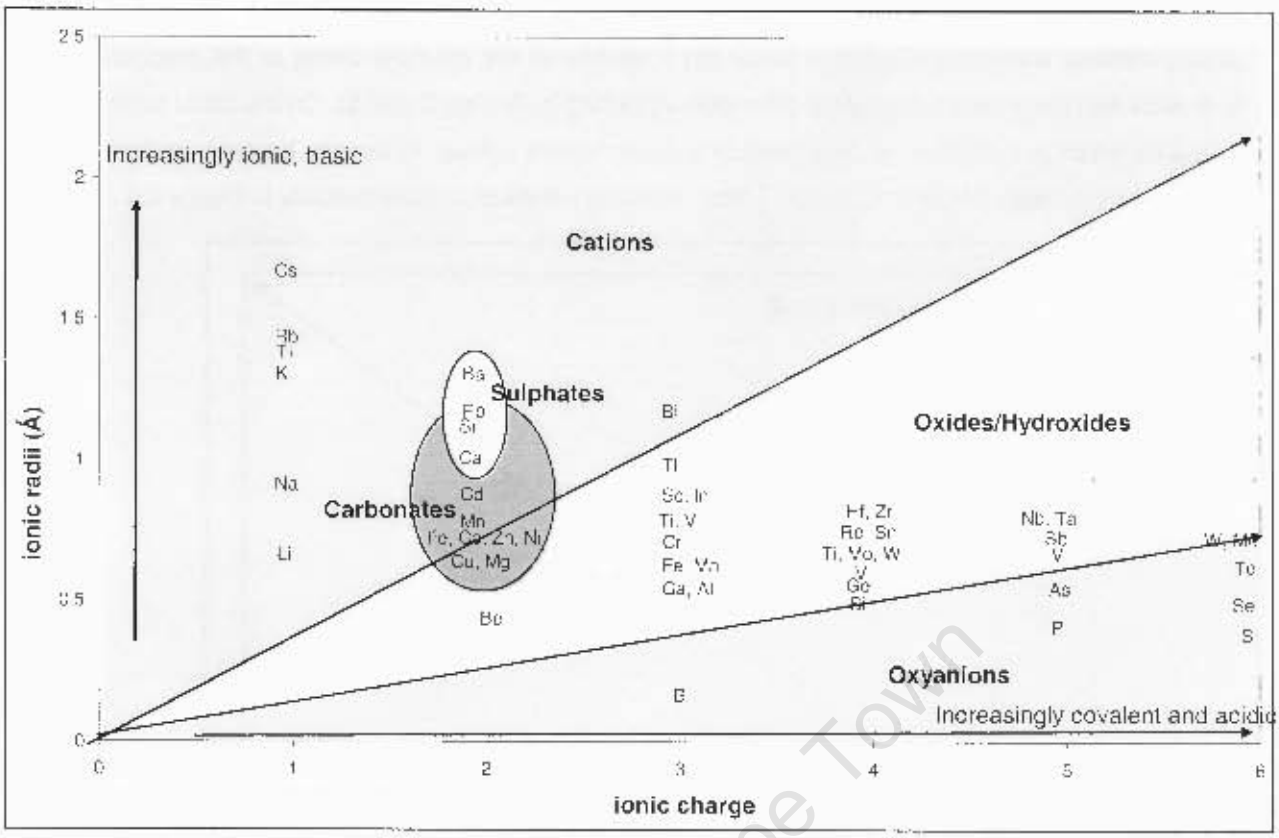


Figure 2.5: Stable forms of the elements under atmospheric conditions on the basis of ionic radii and charge density (modified from Cox, 1995)

The plot of ionic charge vs. ionic radii in Figure 2.5 indicates that the elements can be divided into a number of groups on the basis of their stable forms and associated solubilities, viz:

- ***Elements forming low-charged cations***: This group includes the relatively large alkali metals, the salts of which are highly basic, ionic and soluble in water.
- ***Elements forming insoluble carbonates and/or sulphates***: This group includes the alkaline earth metals and many of the 1st row transition elements, the oxides and salts of which are relatively soluble in the absence of carbonate and sulphate. These elements form relatively insoluble compounds with doubly charged anions such as carbonate and sulphate.
- ***Elements forming partially to sparingly soluble oxide/hydroxides***: Elements falling into this group are of intermediate size and charge density (Z= 3 or 4) and include some of the first row, as well as many of the 2nd and 3rd row transition elements. These elements are partially to sparingly soluble in water.
- ***Elements forming oxyanions***: These elements are small and highly charged (Z = 5 or 6), and their salts are relatively soluble in water.

The prediction of stable element forms and associated solubilities under disposal conditions on the basis of ionic radii and charge density is, however, largely qualitative and very general. For many of the elements, the solubility of their stable compounds will be dependent on parameters such as complexing

ions and, in particular, pH. In accordance with Jones (1995), the general solubilities of elements which display cationic chemistry in solution below pH 9 decline as the pH rises owing to the precipitation of hydroxide and carbonate compounds (elements occurring in Groups 2 and 3). On the other hand, those elements which are present as oxyanions in surface waters (Group 4) tend to be more mobile in the neutral to moderately alkaline pH range. These trends are illustrated schematically in Figure 2.6.

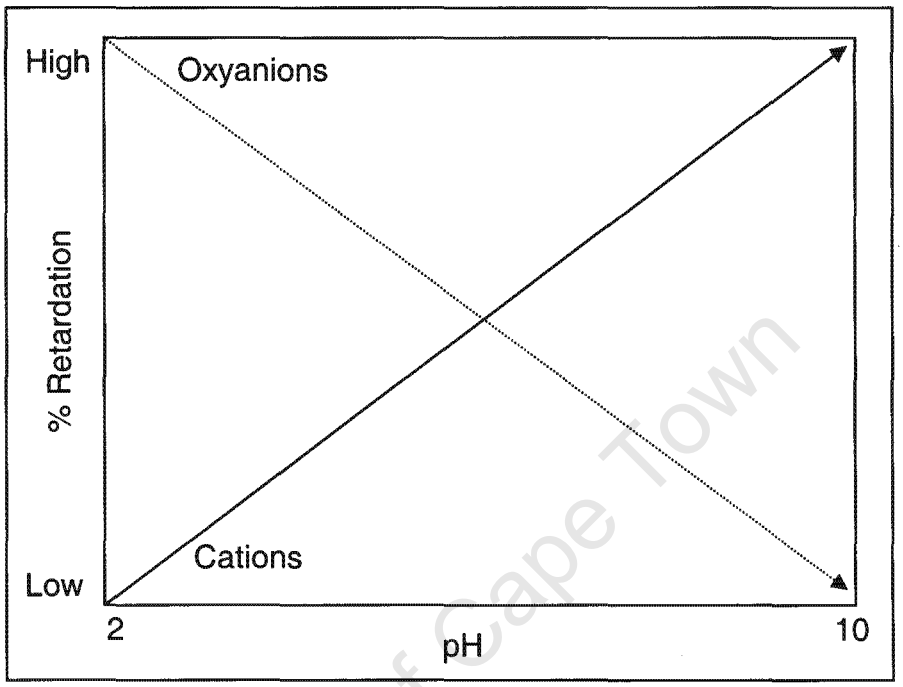


Figure 2.6: Schematic illustration of the effects of pH on retardation of metal mobilities (Jones, 1995)

Another important parameter influencing the dissolution/precipitation behaviour of those elements which occur in more than one stable oxidation state under typical atmospheric conditions (e.g. Fe, Mn, Cr, As, V, Mo and W), is the redox potential (Eh). Changes from one oxidation state to another involve the transfer of electrons in *reduction-oxidation* or *redox* reactions, the potential for which is measured by equilibrium electrode potential differences (Eh). As indicated in Figure 2.7, the properties of both naturally occurring and contaminated water sources vary quite considerably, encompassing a number of broad Eh (reducing, transitional and oxidising) and pH (strongly acidic, weakly acidic, neutral, weakly alkaline and strongly alkaline) regions.

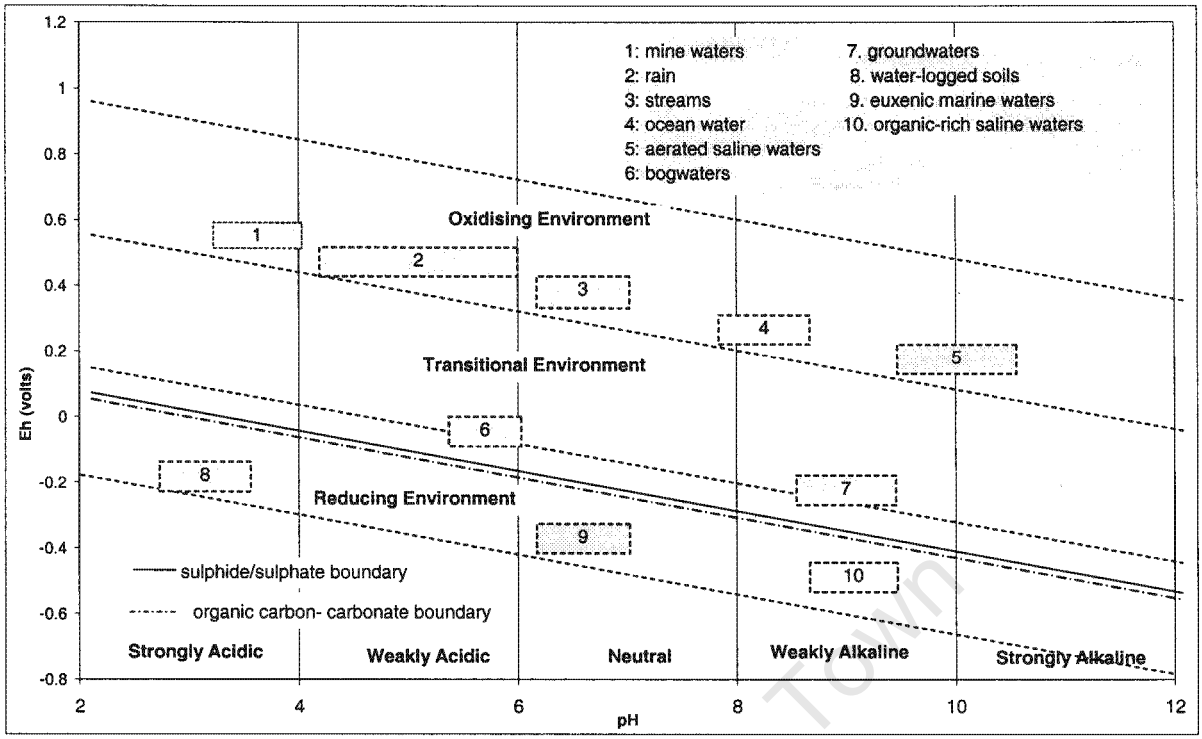


Figure 2.7: Generic Eh-pH diagram for water sources (Garrels, 1960 and Brookins, 1988)

The effect of variations in the stable forms, and likely dissolution/precipitation reactions, as a function of pH and redox potential, can be derived from Eh-pH diagrams, which identify regions of dominance for the different chemical forms in which individual elements may occur as a function of redox potential and pH. On the basis of published Eh-pH diagrams for the elements under typical weathering conditions (Brookins, 1988) a speciation model has been constructed in Table 2.6, indicating the thermodynamically stable forms of associated elements within typical Eh and pH value ranges. Yet another parameter influencing the dissolution/precipitation behaviour of elements is the chemical composition of the leach solutions, particularly in terms of the nature and concentration of major soluble ions (ionic strength). High concentrations of soluble ions (high ionic strength) can increase the mobility of trace to minor elements by competing for adsorption sites and by forming soluble complexes. Major soluble ions can also serve to immobilise trace to minor elements, through the formation of insoluble compounds such as metal carbonates and sulphates.

Apart from dissolution/precipitation and redox reactions, as controlled largely by pH and Eh respectively, the process of *adsorption/desorption* can also be important in the release of elements from waste deposits. According to Eary et al (1990) adsorption/desorption reactions can be ignored in cases where the chemical release is controlled by rapid dissolution/precipitation of sparingly to partially soluble compounds (solubility controlled). However, in the case of highly soluble salts or kinetically slow dissolution/precipitation reactions, adsorption reactions can significantly influence the mobility of contaminants even to the point of virtual immobilisation.

Table 2.6: Eh-pH speciation model

A: Transitional redox potential

	pH 4-6	pH 6-8	pH 8-10
Stable oxides	Zr(IV)-Hf(IV)-Ti(IV)-Sn(IV)-Nb(V)-Ta(V)-Sb(V)	Zr(IV)-Hf(IV)-Ti(IV) -Sn(IV)-Nb(V)-Ta(V)- Sb(V)	Zr(IV)-Hf(IV)-Ti(IV)- Sn(IV)-Nb(V)-Ta(V)- Sb(V)
Oxides/hydroxide precipitates	Be(II)-Al(III)- Ga(III)- Sc(III)-Si(IV)-Ge(IV)	Be(II)-Al(III)- Ga(III)- Sc(III)-Si(IV)-Ge(IV-Fe(III)- In(III)-Bi(III) Cr(III)-V(III)/(IV)	Be(II)-Al(III)- Ga(III)- Sc(III)-Si(IV)-Ge(IV-Fe(III)- In(III)-Bi(III) Cr(III)-V(III)/(IV)
Metals	Au-Ag-PGMs-Hg-Se-Te	Au-Ag-PGMs-Hg- Se-Te	Au-Ag-PGMs-Hg- Se-Te-Cu
Sulphates	Ca(II)-Sr(II)-Pb(II)-Ba(II)	Ca(II)-Sr(II)-Ba(II)	
Carbonates		Pb(II)-Mn(II)-Fe(II)	Cd(II)-Co(II)-Sr(II)-Ca(II)-Pb(II)
Soluble cations	In(III)-Bi(III)- Cr(III)-V(III)/(IV) Tl(I)-Ni(II)-Co(II)-Zn(II)-Cd(II)-Cu(II)-Mg(II)-Fe(II)-Mn(II)-alkali metals	Tl(I)-Ni(II)-Co(II)-Zn(II)-Cd(II)-Cu(II)-Mg(II)-Fe(II)-Mn(II)-alkali metals	Ni(II)-Co(II)-Zn(II)-Cd(II)-Cu(II)-Mg(II)-Fe(II)-Mn(II)-alkali metals
Soluble oxyanions	B(III)-P(V)-As(V)-S(VI)-Re(VII)-Mo(VI)-W(VI)	B(III)-P(V)-As(V)-S(VI)-Re(VII)-Mo(VI)-W(VI)	B(III)-P(V)-As(V)-S(VI)-Re(VII)-Mo(VI)-W(VI)

B: Oxidising redox potential

	pH 4-6	PH 6-8	pH 8-10
Stable oxides	Zr(IV)-Hf(IV)-Ti(IV)-Sn(IV)-Nb(V)-Ta(V)-Sb(V)	Zr(IV)-Hf(IV)-Ti(IV)-Sn(IV)-Nb(V)-Ta(V)-Sb(V)	Zr(IV)-Hf(IV)-Ti(IV)-Sn(IV)-Nb(V)-Ta(V)-Sb(V)
Stable oxides/hydroxide precipitates	Be(II)-Al(III)- Ga(III)- Sc(III)-Si(IV)-Ge(IV)	Be(II)-Al(III)- Ga(III)- Sc(III)-Si(IV)-Ge(IV-Fe(III)- In(III)-Bi(III)-Hg-PGMs	Be(II)-Al(III)- Ga(III)- Sc(III)-Si(IV)-Ge(IV-Fe(III)- In(III)-Bi(III)- Hg-PGMs
Metals	Au	Au	Au
Sulphates	Ca(II)-Sr(II)-Pb(II)-Ba(II)	Ca(II)-Sr(II)-Ba(II)	
Carbonates		Pb(II)-Mn(II)-Fe(II)	Cd(II)-Co(II)-Sr(II)-Ca(II)-Pb(II)- Ni(II)-Zn(II)-Mg(II)
Soluble cations	In(III)-Bi(III)- Cr(III)-V(III)/(IV) Tl(I)-Ni(II)-Co(II)-Zn(II)-Cd(II)-Cu(II)-Mg(II)-Fe(II)-Mn(II)-alkali metals-Ag- PGMs	Tl(I)-Ni(II)-Co(II)-Zn(II)-Cd(II)-Cu(II)-Mg(II)-Mn(II)-alkali metals-Ag(I)	Tl (I)-Ni(II)-Zn(II)-Mg(II)-Ag(I)-Mn(II)-Cu(II)-alkali metals
Soluble oxyanions	B(III)-P(V)-As(V)-S(VI)-Re(VII)-Mo(VI)-W(VI)-Se-Te	B(III)-P(V)-As(V)-S(VI)- Re(VII)-Mo(VI)-W(VI)-Cr(VI)-V(V)-Se(IV)-Te(IV)	B(III)-P(V)-As(V)-S(VI)-Re(VII)-Mo(VI)-W(VI)-Cr(VI)-V(V)-Se(IV)-Te(IV)

Adsorption is a phase distribution process whereby the dissolved ionic species are transferred from the liquid phase onto solids with large, charged surfaces, including hydroxide/oxyhydroxide compounds of metals such as aluminium, iron, titanium, manganese and zirconium, carbonate compounds, clays and organic colloids (Bourg, 1995; Thornton, 1983). Adsorption/desorption reactions are influenced by a number of parameters, including the ionic charge of the element being adsorbed; pH and ionic strength

of the solution; and the surface properties of the adsorbing solids (Bourg, 1995). In general the adsorption of metal cations will decrease as the concentration of H^+ ions and soluble cationic salts (alkali and alkaline earth metals) increase, due to competition between these ions and metal ions for the negatively charged exchange sites on organics and inorganics (Parametrix, 1995). The pH of the solution has a significant effect on the adsorption of metal cations as H^+ ions are relatively strongly adsorbed. Similarly, the adsorption of metal oxyanions will decrease as the pH and the soluble anionic salt (chloride, nitrate, sulphate) concentrations increase. Some of the commonly occurring major secondary solids, and metals ions adsorbed by them, are presented in Table 2.7.

Table 2.7: Common metal-solid adsorption associations (Thornton, 1983)

Adsorbing solid	Adsorbed metal
Iron oxides	V, Mn, Ni, Cu, Zn and Mo
Mn oxides	Fe, Co, Ni, Zn, Pb
Carbonates	V, Mn, Fe, Co, Cd
Clays (silicate minerals)	Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb

Adsorption/desorption reactions are generally rapid and can be considered to be at equilibrium, i.e. rate of the forward and reverse reactions are the same, and there is no bulk change in the reactants and products. Many dissolution/precipitation and in, particular, reduction/oxidation reactions, are however, limited by slow kinetics, and are unlikely to be at equilibrium within a waste deposit.

In summary, the chemical reactions involved in the mobilisation of elements in a solid waste deposit can be sub-divided into the following generic types of controlling mechanisms:

- ***Distribution-controlled dissolution reactions***: In cases where the element is present in a form which is highly soluble under the conditions of leaching, and the rate of the dissolution reaction is rapid, the dissolution of the element within the waste deposit will be largely determined by its abundance or total concentration and mode of occurrence within the deposit i.e. the mobility or chemical availability of the element can be said to be distribution-controlled. In general mineral phases and their associated elements that are enriched on particle surfaces will be more available than those incorporated predominantly in sparingly soluble phases.
- ***Solubility-controlled dissolution/precipitation reactions***: In cases where the element is present in a form which is only sparingly to partially soluble under the conditions of leaching, and the precipitation/dissolution reaction rates are relatively rapid, the extent of dissolution will be largely determined by the solubility of the compound as a function of pH and, to a lesser extent, complexing ions i.e. the mobility of the element can be said to be solubility-controlled. This is often the case for those elements forming sparingly to partially soluble hydroxides and sulphate compounds, as their dissolution/ precipitation rates are generally rapid.

- ***Sorption-controlled reactions***: Sorption-controlled reactions include those reactions where the mobility of the element is largely determined by rapid and reversible adsorption/desorption reactions. Availability is only likely to be sorption-controlled in cases where the element is present in a form which is highly soluble, or for which dissolution/precipitation occurs relatively slowly. Sorption-controlled reactions are influenced by a number of 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.
- ***Kinetically-controlled reactions***: In cases where the rates of the reactions governing the mobility of elements are slow, then the chemical availability can be said to be kinetically-controlled. Most redox speciation reactions are extremely slow, with the majority of redox couples existing in a state of disequilibrium. Other examples of kinetically slow reactions include the dissolution of silicate minerals and relatively inert simple oxides (e.g. ZrO_2); and the precipitation of carbonate compounds as a result of CO_2 diffusion into the waste pile.

2.2.2 Chemical behaviour of solid wastes from the mineral-based resource industries

Despite the complexities, particularly in terms of the vast number of variables associated with any particular solid mineral waste disposal system, it is postulated that the number of strategic elements of environmental significance, and the mechanisms and parameters controlling their release, is likely to be relatively limited and similar for a wide range of waste types and disposal scenarios. This sub-section identifies the chemical processes and parameters which are likely to be involved, and of those, which are likely to have the greatest effect on the availability of solid waste constituents in a disposal scenario.

Solid wastes arising from mining and metallurgical operations will not be at equilibrium with the conditions on the disposal site, and will thus be altered by chemical or biochemical weathering reactions. The process of chemical weathering can be considered as an attempt to attain equilibrium in a system composed of air, minerals and water, ultimately resulting in a deposit of secondary solids which are stable under the disposal conditions. Alterations to major phases as a result of weathering or microbial activity can influence the availability of trace to minor contaminants 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. The inter-relationship of the major and minor phases and the factors controlling their behaviour within solid mineral deposits is illustrated in the conceptual chemical behaviour model presented in Figure 2.8.

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 dependent 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).

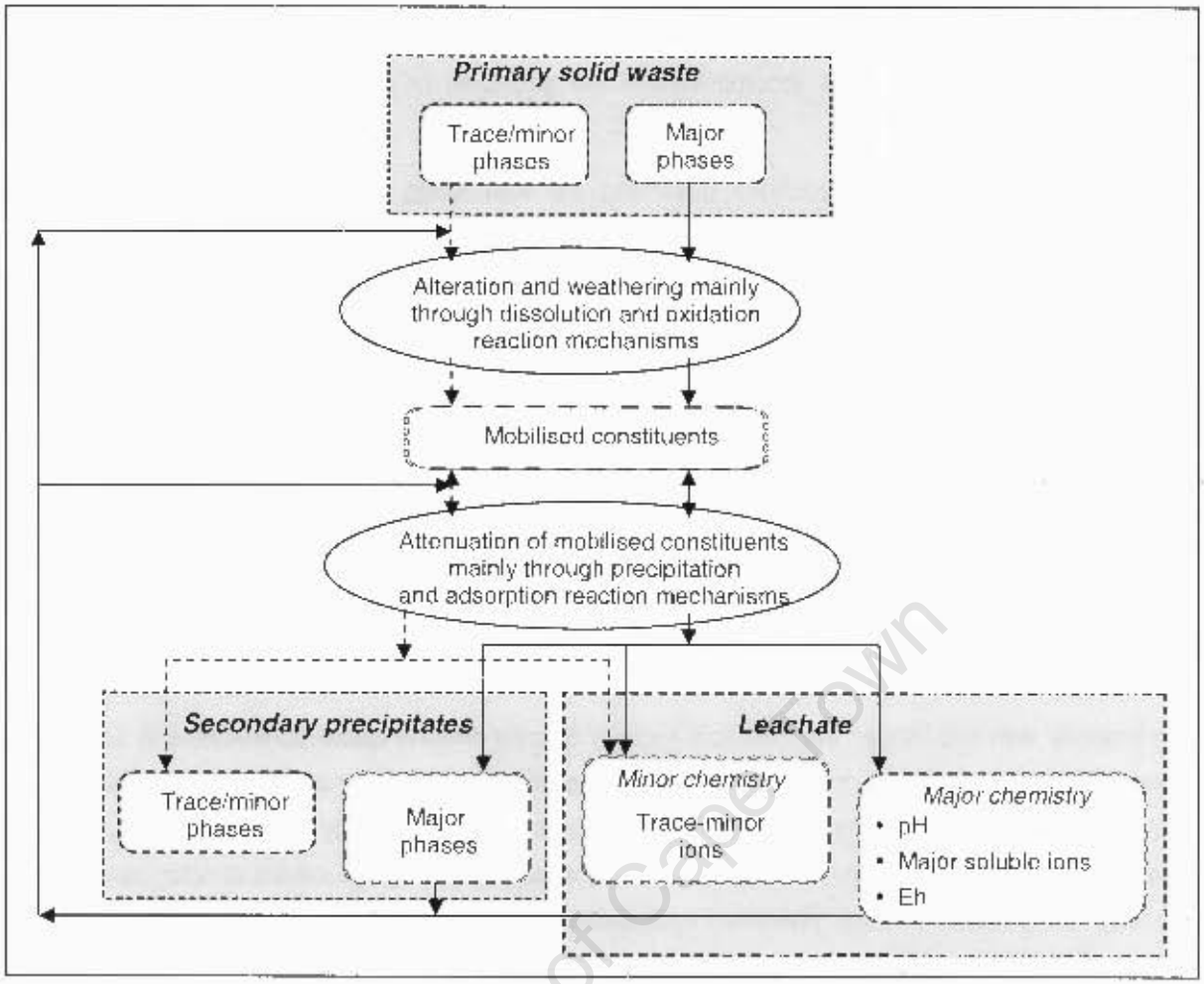


Figure 2.8: Conceptual model of the chemical behaviour of solid mineral waste constituents

On the basis of this understanding, the waste-specific properties considered to be of key significance in terms of predicting and prioritising the potential chemical availability of solid mineral waste constituents include:

- ***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 dependent 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.

- ***Compositions and weathering chemistry of major phases in the waste***: As indicated in Figure 2.8, alterations to major phases as a result of weathering or microbial activity can have a significant influence on the availability of trace to minor constituents and the nature of leachate generated. Of particular relevance are the major phases and reaction mechanisms influencing the redox potential, major soluble ions, nature and concentration of secondary solids and, in particular, pH.

2.3 Predicting key constituents of potential environmental significance

Apart from enabling the potential environmental risks associated with solid mineral wastes to be linked back to the feed ores and waste generating processes, the criteria developed above can also be used to screen and prioritise potentially strategic constituents[5], thereby serving to guide more detailed risk assessment studies (e.g. empirical waste characterisation and/or predictive modelling). 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.

[5] In the context of this study, strategic constituents are those constituents which are considered to be of key environmental significance both in terms of their presence in the waste and their impact on the environment.

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. A number of ranking and scoring systems have 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). Discussions in the previous sections of this chapter indicate, however, that such criteria are generally not sufficient for evaluating and prioritising the environmental risks associated with metal-bearing solid wastes for the primary mineral-based resource industries. In particular:

- the majority of the constituents are naturally-occurring and can result from non-anthropogenic sources.
- many of the constituents are essential elements, and there is a threshold for both deficiency and excess.
- the toxicity of metallic constituents will be dependent on their speciation.
- the availability and speciation of trace metals are controlled by local conditions, such as the pH, Eh and concentrations of the complexing ions in the pore waters, rather than their intrinsic properties.

This section starts by developing a conceptual and generic approach for screening and ranking the potentially strategic constituents in solid mineral wastes, on the basis of the hazard potential and availability criteria identified in Sections 2.1 and 2.2 respectively. Feasible and available tools for the generation of input data which enable the conceptual model to be translated into a quantitative numerical model are subsequently assessed in sub-sections 2.3.2 (hazard potential) and 2.3.3 (availability).

2.3.1 Conceptual methodology

On the basis of the qualitative understanding developed in Section 2.1, 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 2.1 and 2.2 respectively.

Effect factor = solid concentration/environmentally acceptable concentration	Equation 2.1

Enrichment factor = solid concentration/typical background concentration	Equation 2.2

Equations 2.1 and 2.2 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 2.3a-b.

Hazard potential factor = (*m.* effect factor).(*n.* enrichment factor)	Equation 2.3a
Hazard potential factor = $(m.n)(\text{solid concentration})^2 / ((m.\text{environmentally acceptable concentration}).(n.\text{typical natural concentration}))$	Equation 2.3b
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 2.3b, 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 2.4.

Risk potential factor $= (m.n)(\text{available solid concentration})^2 / ((m.\text{environmentally acceptable concentration}).(n.\text{typical natural concentration}))$	Equation 2.4

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 2.5a-b.

Availability potential factor = predicted extent of mobilisation (mass %)/100	Equation 2.5a
Available concentration = (availability potential factor).(total solid concentration)	Equation 2.5b

A systematic and iterative procedural framework for the identification and quantification of potentially strategic waste constituents is depicted in Figure 2.9.

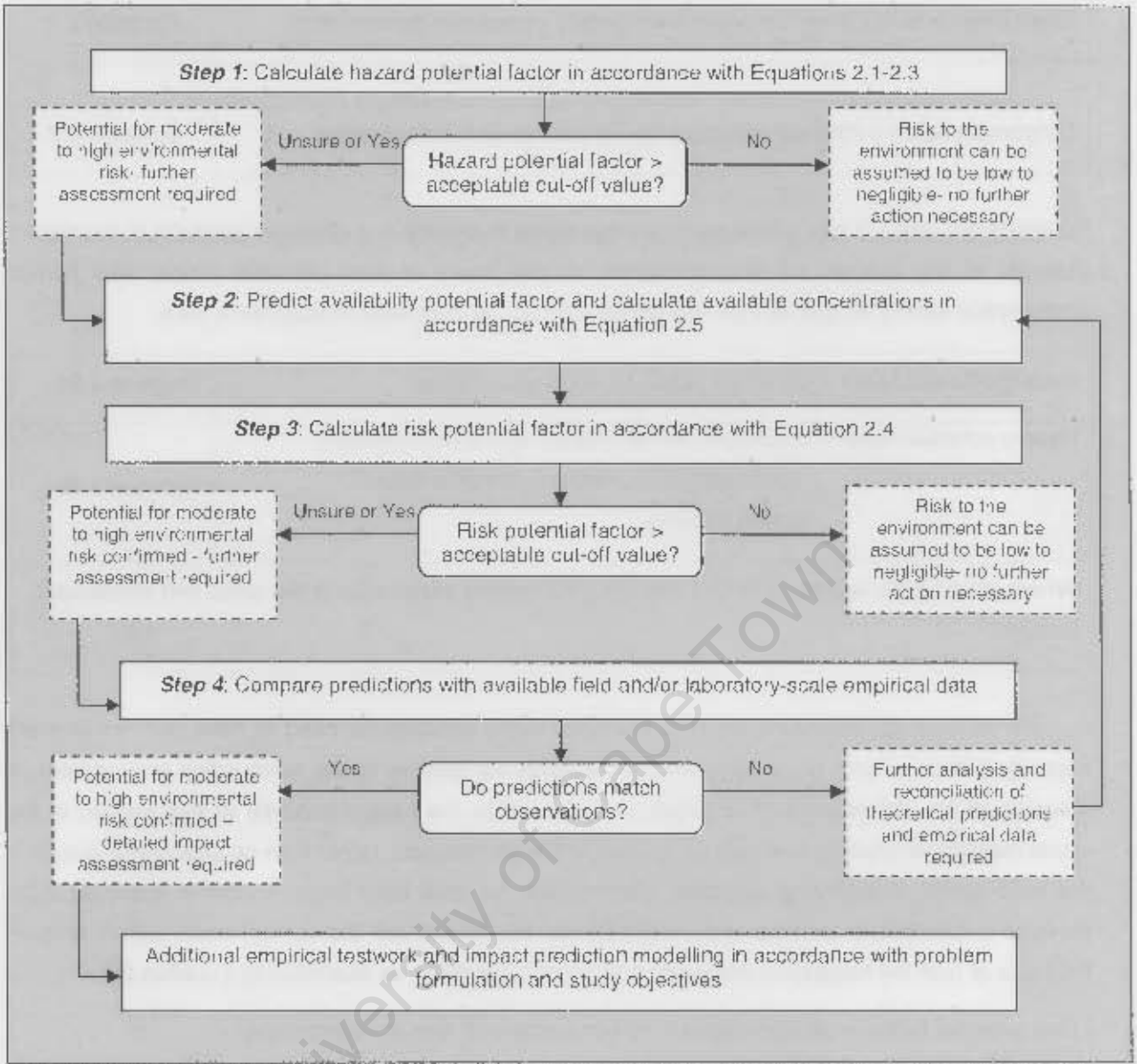


Figure 2.9: Iterative procedural framework for the screening of potentially strategic constituents in solid mineral wastes

This framework represents a methodology algorithm 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. It is, however, important to bear in mind that the so-determined hazard, mobility and risk potential factors are relative rather than absolute measures, and have been specifically developed to compare and rank the various waste constituents in accordance with environmental significance, rather than provide an indicator of actual impact. In this regard, the units of measurement are not usually important as long as they are consistent.

2.3.2 Predicting the hazard potential factor

As discussed in Section 2.1, 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 2.1, 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 2.2. On this basis, concentration levels which are likely to be of significance in terms of hazard potential have been estimated, and the elements ranked accordingly, in Table 2.8.

This generic screening is based on the hazard potential only, and does not take into account the mobility of waste constituents i.e. calculated concentration levels should be considered as being representative of *available* concentrations. Detailed quantitative data is presented in Appendix 2.3.

Table 2.8: Generic ranking of environmentally significant concentration levels for solid mineral waste constituents on the basis of their hazard potentials

Group description	Estimated environmentally significant available concentration levels (mg/kg)	Elements
I: Potential for environmental risk if present at very low (trace) available concentration levels	< 10	Te < Hg < Ag < Cd , Re < Se < In < Pt < Tl < Sb < As < Au< Mo
II: Potential for environmental risk if present at low (minor) available concentration levels	10-100	Pb, Bi < Be << Ge < Ni, U < W
III: Potential for environmental risk if present at moderate available concentration levels	100-1000	Sn, I< Co< Ta< Mn, B, Cr < Cu < Hf < REE << Zn< Br < Ba < Ga < Zr < Nb < V
IV: Potential for environmental risk only if present at relatively high available concentration levels	A: 1000-10 000 B: >10 000	A: F < Sc < Li < Cl < Rb < Fe, Al < Ti < Sr < S < P B: Si < Mg < Na < K < Ca

Calculations:

Hazard potential factor = $(m.n)(\text{solid concentration(ppm)})^2 / [(m.\text{water quality criteria (ppm)}).(n.\text{average crustal abundance (ppm)})]$.....Equation 2.3b

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 hazard potential factors ≥ 1000

The results in Table 2.8 confirm that many of the scarce, chalcophilic elements (e.g. Te, Hg, Ag, Cd) may pose a significant risk to the environment, even if released from solid waste deposits at relatively low concentration levels (see discussions in Section 2.1). In contrast, individually, the soluble salts (mainly sulphates, chlorides, bicarbonates and, to a lesser extent, nitrates and phosphates) of the major cations calcium, magnesium, sodium and potassium are unlikely to be present in high enough concentrations to pose a risk to the environment. Cumulatively, however, salts may cause significant environmental problems. For this reason, soluble salts are normally expressed in terms of salinity, using either TDS (Total Dissolved Salts) or EC (Electrical Conductivity) as quantitative measures, and guideline values for individual salt ions are generally considered unnecessary.

2.3.3 Predicting the availability potential factor

In accordance with the chemical behaviour model developed in Section 2.2, 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 2.6).

Availability Potential Factor = Reactivity potential factor x (1-attenuation potential factor)	Equation 2.6

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.

The prediction of available concentration levels and potential risk factors (steps 2 and 3 of the procedural framework for the identification and quantification of potentially strategic waste constituents as presented in Figure 2.9) can thus be sub-divided into two stages (a and b) as illustrated in Figure 2.10.

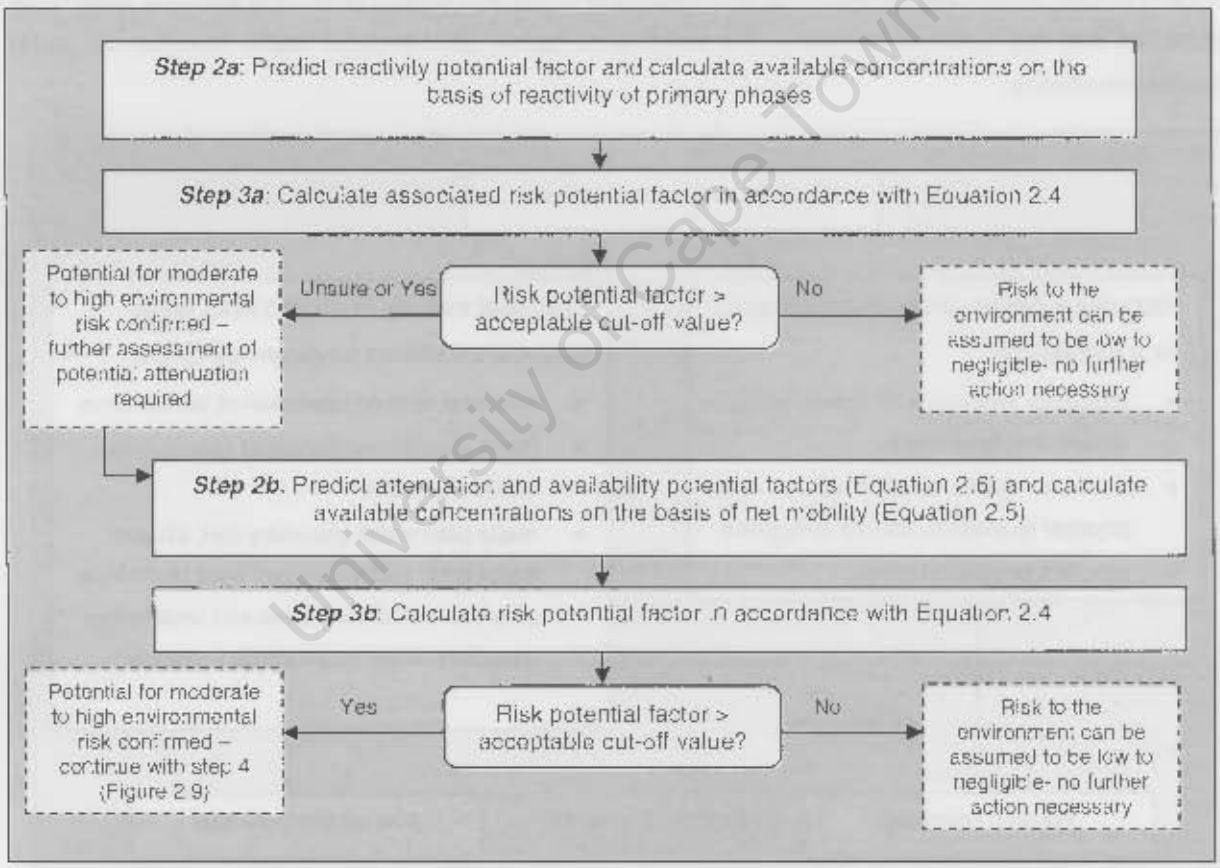


Figure 2.10: Procedural framework for predicting potential chemical availability and associated risk potential of solid waste constituents

In contrast to hazard potential, which is largely specific or inherent to a particular chemical species, the mobility of solid waste constituents is influenced by a large number of variables. 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. An overview of some of the appropriate tools, as well as generalised guidelines in terms of their selection and application, is provided within Chapter 5 of the thesis.

2.4 Summary and concluding remarks

In this chapter of the thesis, the criteria of key significance in terms of predicting the potential impacts and risks associated with solid mineral wastes in a disposal scenario have been identified, and a generic protocol for the screening and ranking of the various waste constituents developed accordingly.

These generic protocols and associated criteria, as summarised in Figure 2.11, have been based on a comprehensive review and fundamental understanding of the key factors governing both the hazardous properties and the chemical behaviour (or mobility) of typical solid mineral waste constituents under disposal conditions.

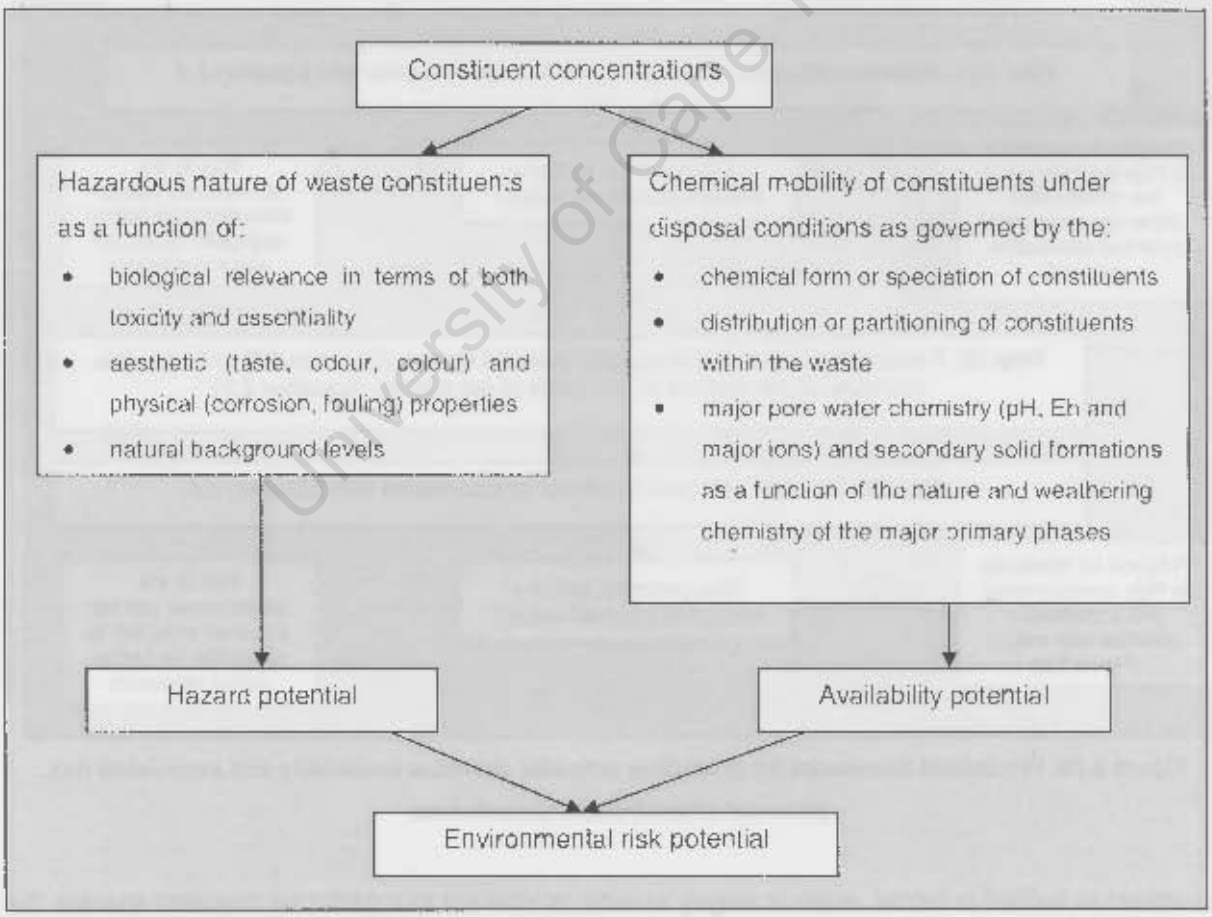


Figure 2.11: A summary of environmentally significant solid waste properties and governing criteria

The generic methodology for the screening and ranking of environmental risks also takes into account those environmental issues of specific relevance to deposits of solid wastes from the primary mineral-based resource industries, viz. salinisation, elevated trace-minor metal concentrations, and extreme pH values. Although designed to generate data and information which is indicative of relative rather than absolute measures of environmental risk, the generic methodology is nevertheless scientifically robust, without being overly complex. As such, it provides valuable knowledge which can, if employed to seek out opportunities and limit risks, play a key role in early design stage decision-making, as well as in guiding and informing further data collection and risk assessment studies in later design stages. Chapter 5 provides technical guidelines pertaining to the selection and application of scientific techniques for predicting the availability potential of solid waste constituents, i.e. for meeting the objective of step 2 of the proposed methodology (see Figure 2.9). Application of the generic criteria and protocols developed within this chapter is demonstrated for the case of typical copper sulphide tailings in Chapter 7 of the thesis.

As indicated in Figure 2.11, the screening and ranking of solid waste constituents in terms of their hazard potential, chemical availability and, ultimately, potential environmental risk, requires prior knowledge of both their concentrations and forms. Criteria for the generation of such information on the basis of the waste origins (feed ore) and source (generating process) is the subject of discussions in Chapters 3 and 4 respectively.

Appendix 2.1: Water quality guidelines

(DWAF, 1996; ANZECC, 1999)

	Domestic use (ppm)		Agricultural use (ppm)				Protection of aquatic ecosystems (ppb)	
			Livestock watering		Crop irrigation			
	ANZECC	SA	ANZECC	SA	ANZECC	SA	ANZECC	SA
Hg	0.001	0.001	0.002	0.001	0.002		0.013	0.04
Ag							0.005	
Cd	0.002	0.005	0.01	0.01	0.01	0.01	0.013	0.15
Sb	0.003	0.05						
As(T)	0.007	0.01	0.5	2	0.1	1	7.6	10
As(III)							1.6	
As(V)							2.4	
Pb	0.01	0.01	0.1	0.1		0.2	1.2	0.2
Se	0.01	0.02	0.02	5	0.02	0.02		2
Se(IV)							1.4	
Se(VI)							2.3	
Ni	0.02		1	1	0.2	0.2	0.7	
Cr(T)								
Cr(VI)	0.05	0.05	1	1	0.1	0.1	1.1	7
Cr(III)		0.5	0.5-5	5			9	12
Mo	0.05		0.05	0.01	0.01	0.01	6.7	
CN	0.08						1	1
Be					0.1	0.1		
Mn	0.1	0.05		10	0.2	0.02	47	180
Al	0.2	0.15	5	5	5		1.2	5
B	0.3	5	5	5	0.5	0.5	4.8	
Fe	0.3	0.1		10	0.2		10	
Ba	0.7	4				1		
F		1	2	2	1			
Cu	1	1		0.5-5	0.2	0.2	0.33	0.3
Co			1	1	0.05		0.24	
U			1		0.01		3.5	
V				1	0.1	0.1	6	
Tl							21	
Sulphate							1	
Ammonia							32	
Zn	2.4	3	20	20	2	1	2.4	2
P							35-50	
Nitrate		6		100			120	
Na	180	100						
Mg							100	
Hardness CaCo3	200							
So4	250	200		1000				
Cl	250	100						
TDS	500	450		1000-3000				
pH	6.5-8.5	6.5-9					6.5-8.3	4.5-9
Increase in cond. (μS/m)							60-500	
Conductivity (mS/m)								550

Appendix 2.2: Typical element concentrations in natural environments

(ANZECC, 1999; Beus & Grigorian, 1977; Chapman & Wang, 2000; Cotton & Wilkinson, 1962; Cox, 1995; Logan & Traina, 1993; Tadessa et al, 1994; US EPA, 1995).

Element	Crustal abundance (ppm)	Uncontaminated soils (ppm)			Soil target levels (ppm)	Freshwaters (ppb)	
		Minimum	Maximum	Average		Minimum	Maximum
Si	277200						10000
Al	81300	5000	10000				
Fe	50000	100	10000			0.480	10000
Ca	36300	15	41000		14000		
K	28300						2300.00
Na	25900						6000
Mg	20900						4000
Ti	4400						
P	1200						
Mn	1000	4	7500	800	201	0.130	0.190
F	600					100	1000
S	520	10	40				5000
Ba	430		200				
Sr	290						
V	150	5	121	21			1.000
Rb	120						
Cl	100	8	130		12000		
Cr	100	1.00	1000	100		0.060	0.390
Zr	100						
Zn	80	2	253	50	39	0.010	10
Ni	75	1.00	517	72	17	0.800	1.000
Cu	55	0.40	400	25	28	0.700	10
Li	30						
Co	25	0.40	170	20	27	0.009	0.200
Nb	19						
Pb	16	2	200	20	18	0.005	10
Ga	15						
Sc	14						
B	10						
Sn	3	0.10	40	20			
Cs	3						
Be	2.8						
Br	2.5						
As	1.8	5	50	7	10	1.000	10.00
Mo	1.5	0.20	20	2	1		
Ge	1.3						
W	1						
I	0.5						2.00
Tl	0.3						0.004
Sb	0.2	1.00	9			0.300	5
Cd	0.2	0.01	2	0.20		0.002	0.009
Bi	0.2				0.12		
Se	0.09	0.05	3	0.40	0.50	0.020	1.000
Hg	0.08	0.01	0.3	0.04	0.03	0.0002	0.100
In	0.07						

Appendix 2.2 continued.....

Element	Crustal abundance (ppm)	Uncontaminated soils (ppm)			Soil target levels (ppm)	Freshwaters (ppb)	
		Minimum	Maximum	Average		Minimum	Maximum
Ag	0.07	0.70	5				
Pd	0.01						
Pt	0.005						
Au	0.004						
Te, Ru, Os, Rh, Ir, Re	0.001						

Appendix 2.3: Generic screening of environmentally significant element concentration levels on the basis of hazard potential

Component	Crustal abundance (ppm) (see Appendix 2.2)	Typical guidelines for drinking water (ppm) (see Appendix 2.1)	Estimated environmentally significant concentration (ppm)
Te	0.001	0.02*	0.1
Hg	0.08	0.001	0.3
Ag	0.07	0.01	0.8
Cd	0.2	0.005	1.0
Re	0.001	1*	1.0
Se	0.09	0.02	1.3
In	0.07	0.05*	1.9
Pt	0.005	1*	2.2
Tl	0.3	0.02*	2.4
Sb	0.2	0.05	3.2
As	1.8	0.01	4.2
Au	0.004	5*	4.5
Mo	1.5	0.05	8.7
Pb	16	0.01	13
Bi	0.2	1*	14
Be	2.8	0.1*	17
Ge	1.3	1*	36
Ni	75	0.02	39
U	1.5	1*	39
W	1	5*	71
Sn	3	5*	123
I	0.5	30*	123
Co	25	1*	158
Ta	1	30*	173
Mn	1000	0.05	224
B	10	0.3	224
Cr	100	0.5	224
Cu	55	1	234
Hf	2.6	30*	279
REE	85	1*	292
Zn	80	3	490
Br	2.5	100*	500
Ba	430	0.7	550
Ga	15	30*	670
Zr	100	5*	700
Nb	19	30*	750
F	600	1	775
V	150	5*	870
Sc	14	100*	1200
Li	30	100*	1700
Cl	100	100	3200
Rb	120	100	3500
Fe	50000	0.1	3900
Al	81300	0.2	4000

3

The Characterisation of Ore Deposits: Establishing the Origins of Solid Mineral Wastes

As pointed out in Chapter 1 of the thesis, the limitations and inconsistencies in currently available data and information pertain not only to solid mineral wastes, but also to the 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.

A review of the general literature pertaining to the formation and classification of mineral deposits (see for example Battey, 1981; Corrins, 1969; Cox, 1995; Niggli, 1954; Thornton, 1983) indicates that, although the compositions of ore deposits are dependent on a number of factors and vary quite considerably, minerals and their component elements do not occur together at random. 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. A fundamental understanding of the key mechanisms and parameters controlling the natural formation of mineral deposits will allow prediction of commonly occurring associations of elements and the relative extents to which such groups will be distributed to, or enriched/depleted in, specific deposits. This in turn will allow for more accurate and detailed descriptions of ore deposits, thereby facilitating predictions of the characteristics of the wastes arising from the processing thereof.

To this end the formation and classification of major mineral deposits, in terms of their chemical compositions, is described in Section 3.1, followed by an assessment of the key mechanisms and parameters controlling the distribution and association of elements within such deposits in Section 3.2. The scientific techniques and methods for the derivation of element enrichment factors and compositions within ore depots on the basis of the knowledge and qualitative information gained through this study are discussed within Chapter 5 of the thesis. Practical application for the case of porphyry-type copper sulphide ores is demonstrated within Chapter 6.

3.1 The formation and classification of major mineral deposits

In order to understand how elements are distributed and associated within specific mineral deposits, we first need to understand how they are distributed within the earth's crust. In accordance with the data presented in Appendix 2.2 of Section 2, and summarised in Table 3.1 below, the distribution of elements in the earths crust is very unequal, with 95% of the crust being made up of only eight elements (O, Si, Al, Fe, Ca, K, Na and Mg). These eight elements occur as common rock-forming minerals comprising mainly silicates and aluminosilicates, containing trace elements as substitutions in the lattice structures. The general picture that emerges is that of small amounts of many elements immersed in a vast abundance of a few. Mineral ore deposits occur when one or more of the trace to minor elements have accumulated, through special concentration processes, in a quantity sufficient to be capable of economic extraction.

Table 3.1: Distribution of elements within the earth's crust (after Cotton and Wilkinson, 1962; Cox, 1995)

Abundance	Element
Major elements > 100 000 ppm	Si
10 000< ppm < 100 000	Al>Fe>Ca>K>Na>Mg
Moderately abundant elements 1000< ppm< 10 000	Ti> P
100≤ ppm ≤1000	Mn > F>S> Ba > Sr> V≈Rb>Cl=Cr=Zr
Minor elements 10< ppm< 100	Zn ≈ Ni > Cu> Li ≈ Co > Nb>Pb ≈ Ga ≈Sc
Trace elements 1< ppm ≤10	B > Sn=Cs ≈ Be ≈ Br> As ≈ Mo ≈ Ge
Scarce elements 0.001< ppm ≤ 1	W≈ I ≈ Tl ≈ Sb = Cd = Bi > Se ≈ Hg ≈ In = Ag> Pd>Pt ≈ Au
≤ 1 ppb	Re, Te, Ru, Os, Ir, Rh

A summary of available information pertaining to the ore deposits associated with primary metal production industries is presented in Table 3.2. This information is largely qualitative and based entirely on available and, for the most part, incomplete empirical data. Nevertheless, such information serves to highlight the complexity of mineral ore deposits for which the targeted metal, although relatively enriched in comparison with average concentrations in the earth's crust, is frequently present as only a minor component. In many cases, ore deposits are comprised mainly of valueless or sub-economic elements and their associated minerals, commonly termed gangue, which are thus a major component of solid wastes from the primary mineral resource industry.

Table 3.2: Ore deposits associated with various primary metal resource industry sectors (after Adamson, 1972; Cox and Singer, 2003; Reuter et al, 2003; Xiao & Laplante, 2004)

Industry sector	Typical ore grade	Major ore components	Commonly occurring minor/trace elements
Non-Ferrous Base Metals			
Copper	1-5% (100-700)	Cu, Fe & S	Ni, *Zn, Ni* , Cd, *Mo*, Hg, Pb, Sb, *Ag, In, Se, Te, Bi*, Tl, *Re, As*, Ge, Ga, *PGM's, Au*
Nickel-sulphide	1-5% (100-500)	Ni, Fe, S	As for copper
Nickel-oxide	1-4% (100-500)	Fe, Ni	Al, Cr, Mn, Zn, Co, Cu
Zinc	3-5% (400-600)	Zn, Fe, S	Ni, Co, Cu, *Cd*, Hg, Pb, Sb, *Ag, In, Bi, Tl*, As, *Ge, Ga, Au*, Mn
Lead	2-6% (1000-4000)	Pb, Fe, S	As for Zn
Non-Ferrous Light Metals			
Aluminium	35% (4)	Al, Fe	Mn, Ti, Cr, Fe, Ga, Cu, Zn
Magnesium	–	Mg, Fe	Al, Mn, B, Ni, Cl, Br
Ferro-Alloys			
Chromium	30-40% (1500-2000)	Cr, Fe	Mg, Al, V, Zn, Mo, Pb, Cd
Manganese	30-40% (300-400)	Mn, Fe	Al, Mg, Co, Ni, Cu, As, Pb
Iron	30-60% (6-12)	Fe	Sn, Mg, Cr, Ti, V, Al, As, *Zn, Pb*
Precious Metals			
Platinum Group Metals (PGMs)	5 g/t (5000)	*Cr* ,Fe, *Cu, Ni*, S	*Ni, Cu, Co*, Fe, As, Au, Ag, Cr, Fe
Gold	4-10 g/t (500-1000)	Au	U, Ti, Zr, Cr, Mn V, B, Fe, As, Cu, Zn, Pb, S , Hg, Ag, *PGM's*
Beach Sands	1% (2)	*Fe*, Ti	Sn, V, Al, Cr, *Zr*, Mn, Nb, Ta, U

- Figures in brackets represent enrichment factors relative to abundance in the earth's crust
- Constituent elements in italics represent metals frequently recovered as by-products

Any investigation relating to solid waste outputs from this industry thus requires a quantitative understanding of the chemical compositions of both the host rock-forming and ore-forming (targeted as well as sub-economic) minerals and component elements.

As demonstrated in Figure 3.1, mineral deposits are formed in the first instance by crystallisation from magmatic melts (magmatic deposits), and subsequent physical and chemical weathering of the magmatic deposits on exposure to air and water (sedimentary deposits).

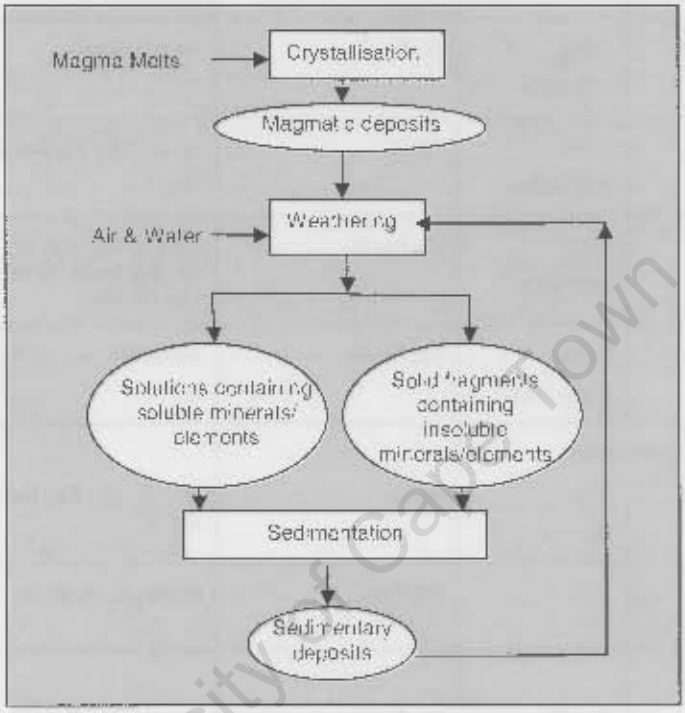


Figure 3.1: Geological and geochemical processes involved in the formation of mineral deposits

Whilst the structures of both magmatic and sedimentary deposits can undergo further transformation or metamorphosis in natural environments, the distinction between metamorphic rocks and those rocks formed by magmatic activity or sedimentation is frequently unclear (Battey, 1981). In general metamorphism entails the stabilisation of mineral components in sedimentary and magmatic rocks mainly as a result of recrystallisation but does not influence the elemental compositions i.e. the compositions of metamorphic deposits generally reflect the compositions of their sedimentary and magmatic precursors. For the purposes of this investigation, attention will be focused only on magmatic and sedimentary deposits.

These magmatic and sedimentary deposits can be grouped or classified in accordance with their bulk chemical compositions and conditions relating to their formation (i.e. their genesis), as indicated in Figures 3.2 and 3.3 respectively. Further information pertaining to the formation and chemical compositions of magmatic and sedimentary deposits is provided in Appendix 3.1

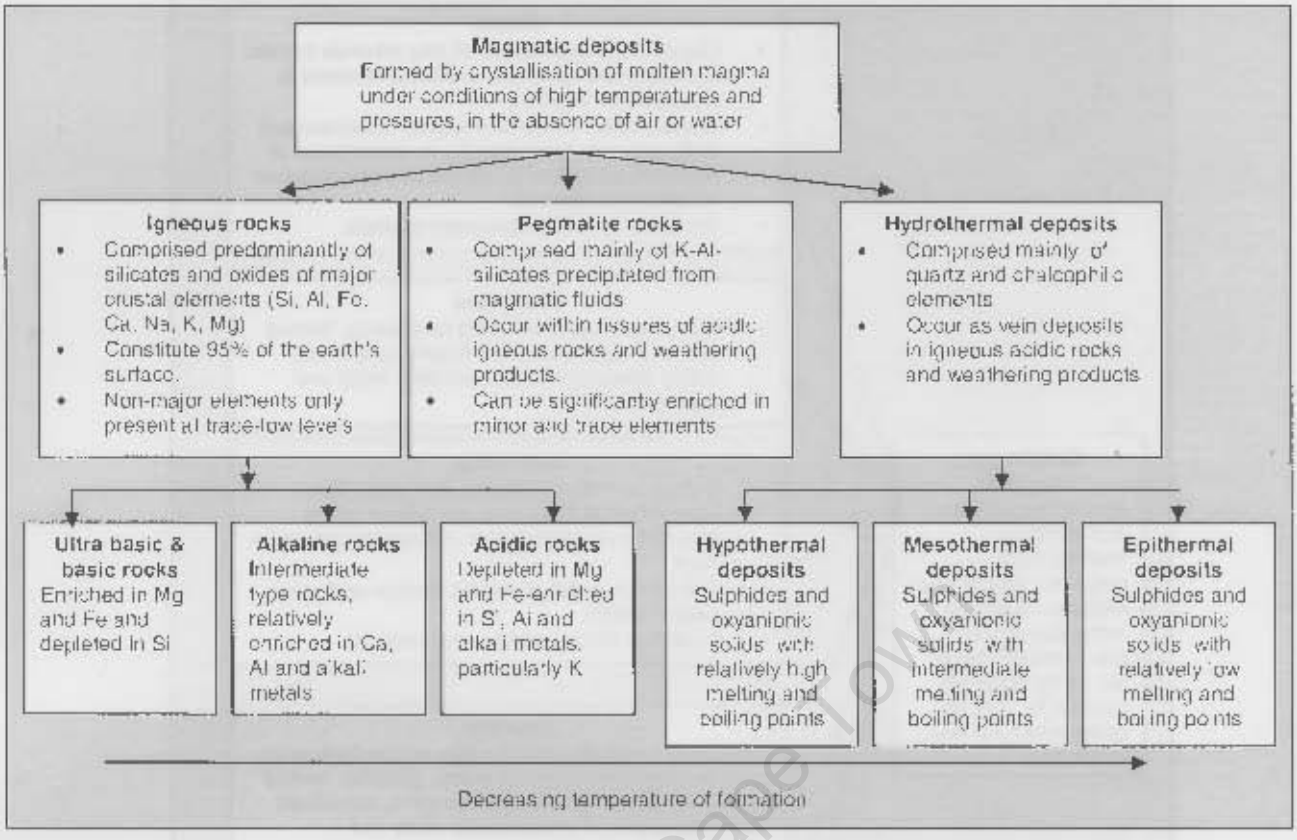


Figure 3.2: Classification of primary magmatic deposits

3.2 The distribution and association of elements in major mineral deposits

A review of general texts on the mineralogy, geology and/or geochemistry of the earth's crust (see for example Batty, 1981; Cox, 1995; Thornton, 1983), indicates that elements occur in the earth's crust in the form of either sulphides (including sulphide analogues such as tellurides, selenides, arsenides and antimonides); oxides (including complex oxides such as silicates, carbonates and sulphates); or as uncombined, native elements.

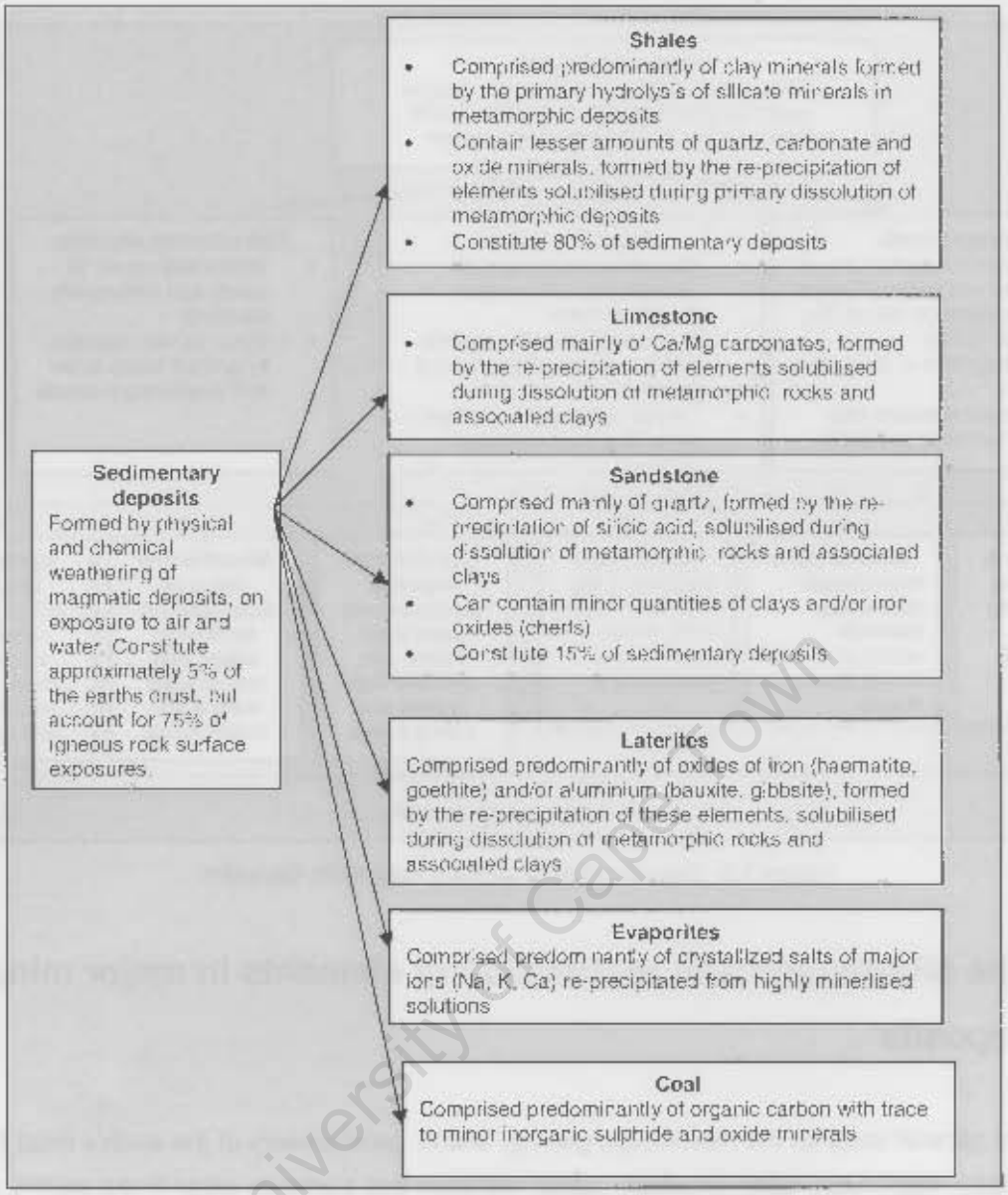


Figure 3.3: Classification of sedimentary deposits

As indicated in Figures 3.4 and 3.5 overleaf, the natural occurrence of elements can, in turn, be correlated with their chemical properties and patterns thereof (as represented by the periodic table), as well as their affinities for oxygen (as measured by the standard Gibbs free energy of oxide formation, ΔG_f°). Metals having a strong affinity for "hard" ligands such as oxides and halides include the strongly-to-moderately electropositive metals, appearing on the left hand side of the periodic table. These elements are commonly termed lithophiles or lithophilic elements. The weakly electropositive metals and semi-metals (or metalloids), appearing in the lower right hand side of the periodic table, have a strong affinity for "soft" sulphide-type (including selenide, telluride, arsenide and antimonide) ligands. These elements only occur as oxides in natural environments under oxidising conditions, and are commonly referred to as chalcophiles. The noble metals (gold, platinum group elements, and, to a lesser extent, copper) frequently occur in the uncombined form, and are commonly referred to as siderophiles.

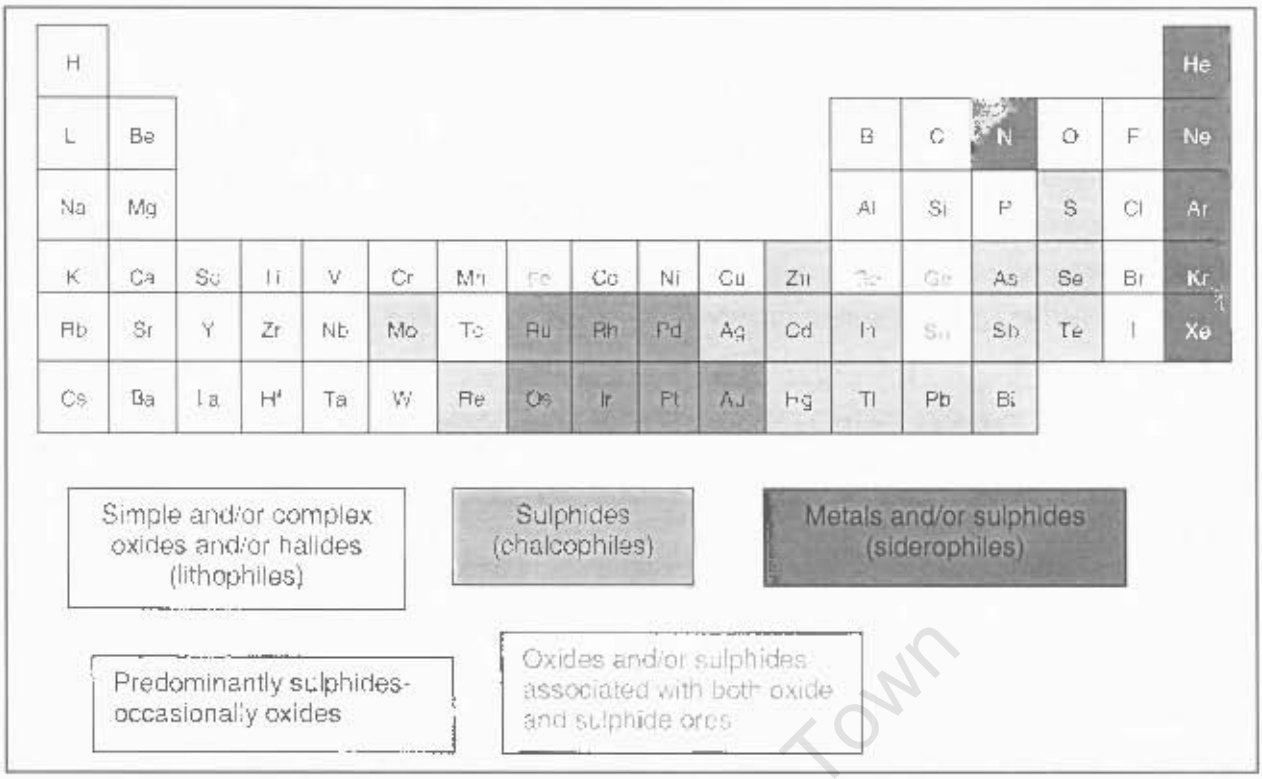


Figure 3.4: Modes of occurrence of elements within the earth's crust (modified from Cox, 1995)

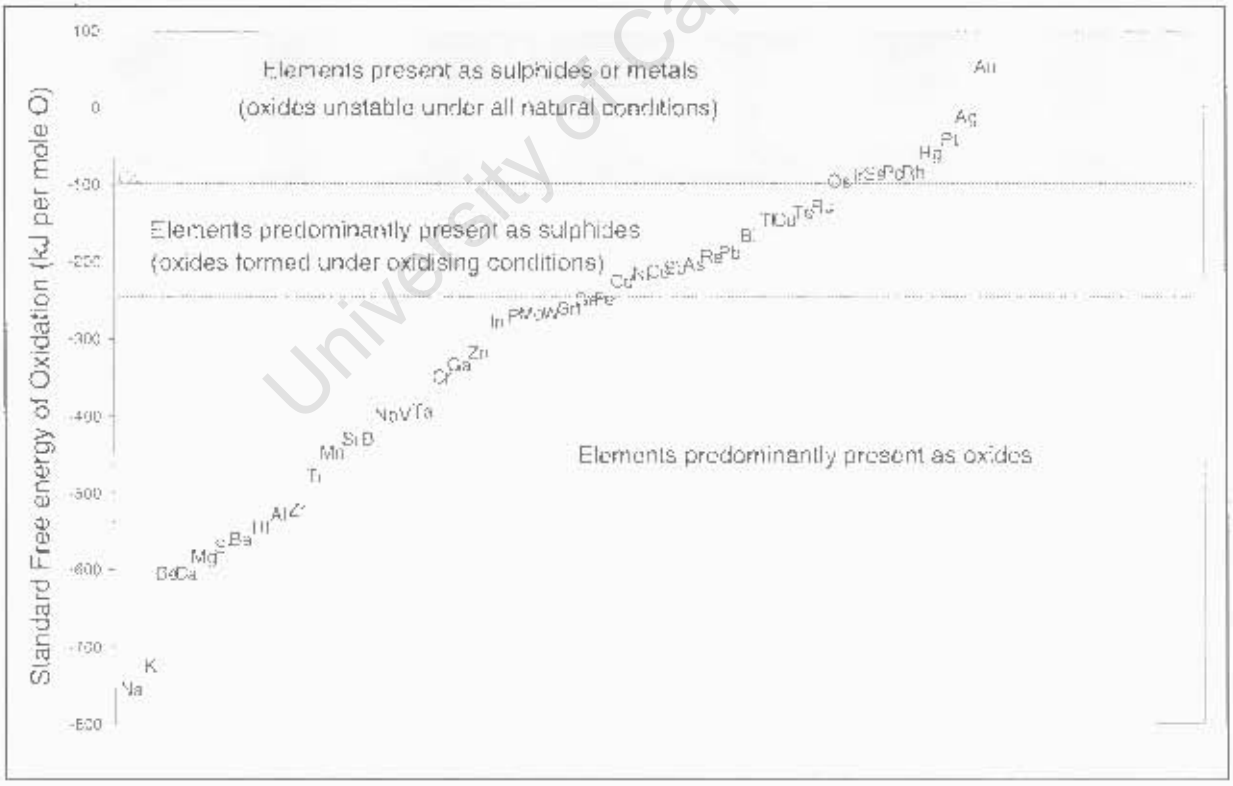


Figure 3.5: The affinity of elements for oxygen (thermodynamic data sourced from Brookins, 1988; Cotton & Wilkinson, 1962; Elliot & Gleiser,1960-63; Garrels, 1960; Knacke et al, 1991; Kneen et al, 1972; Lide, 1997; Price. 1998; Woods & Garrels, 1987; Zelmack, 1992)

The distribution and associations of elements in naturally occurring mineral deposits (ores and host rocks) is thus dictated in the first place by the relative affinities of the elements for hard "oxide-type" versus soft "sulphide-type" ligands, and ores are frequently classified as sulphide or oxide ores, in accordance with the form of the valuable or targeted metals. This classification system is useful to both exploration geologists and process design engineers as it corresponds with behaviour patterns of elements during both the formation and subsequent beneficiation of ore deposits. Some of the physio-chemical properties typical of oxide and sulphide forms of the naturally occurring elements are outlined in Table 3.3.

Table 3.3: Generic properties of oxide and sulphide chemical forms

Property	Oxide compounds	Sulphide compounds
Nature of bonds	Essentially ionic, although the degree of ionic bonding varies according to the electronegativity and ionic charge of the cation.	Essentially covalent-frequently displaying significant metal-metal bonding.
Thermal stability	Will vary according to the ionic nature of the bonds. Generally more stable, with higher melting and boiling points, than sulphide forms.	Relatively unstable-converted to oxides or elemental phases in the presence of oxygen at elevated temperatures.
Solubility	Varies quite considerably in accordance with the nature of the bonds.	Generally stable to hydrolysis and relatively insoluble in water. Dissolution generally requires strongly acidic and/or oxidising conditions.
Physical properties	Generally less dense and harder than sulphides.	Frequently displaying metallic character- high conductivity

The information provided by such a classification system in terms of the physio-chemical properties, behaviours, and associations of elements occurring within any particular ore deposit is, however, both extremely general and broad. The actual properties or characteristics of ores occurring in each class (i.e. suphide and oxide ores) will vary quite considerably, due to the large number of mechanisms and parameters influencing the distributions and associations of elements within naturally occurring mineral deposits. Even in terms of the forms, many elements (such as iron, cobalt, nickel and copper) show intermediate character and can occur as either oxides or sulphides (see Figure 3.4), depending on the environmental conditions. Copper can also occur as native copper.

A detailed review and analysis of the key factors influencing the distribution and association of elements in sulphide and/or oxide type deposits is carried out in the following sub-sections- firstly under the reducing thermal conditions associated with magmatic activities (Section 3.2.1), and secondly under the mildly oxidising aqueous conditions associated with subsequent weathering and sedimentation activities (Section 3.2.2).

3.2.1 Primary magmatic deposits

In the case of primary magmatic deposits, the deportment of minor and trace elements will be governed mainly by crystallisation and ionic substitution reactions.

Crystallisation reactions

The temperatures at which the elements crystallise from magma melts will be influenced largely by the stable forms of the elements and their thermal properties (particularly in terms of viscosities and volatilities) under high temperature, reducing conditions. In general, the sulphide minerals have lower boiling and melting points and are less thermally stable than the oxide phases (simple and complex oxides). Sulphide minerals and their associated chalcophilic and siderophilic elements are thus crystallised from magmatic fluids and condensed vapours after deposition of the relatively stable oxide minerals formed by many of the lithophilic elements, and typically occur as enriched veins or massive local deposits in fissures of acidic host rocks. The thermal stabilities of the ionic oxide phases, and hence the temperatures at which the lithophilic elements crystallise from the magma melts, will, however, vary quite considerably. As discussed by Kneen et al (1972), the thermal properties of oxide compounds are dependent largely on the ionic nature and the basicity of the bonds which can, in turn, be correlated with the ionic radii and charge (or oxidation state) of the cations. In general, the thermal stabilities, and hence the melting points and boiling points, of the oxidic forms of the elements decrease as the ionic charge density (ionic charge (Z)/ ionic radii) of the cations increase. Clearly oxides formed by ions with similar charge densities can be expected to have similar thermal properties, and thus be highly miscible or closely associated under high temperature conditions, such as those occurring during magmatic activity. The effect of charge density on the likely associations of oxides within the various types of magmatic deposits is indicated in Figure 3.6. On the basis of charge densities, an "oxide miscibility model" has been constructed in Figure 3.7 indicating feasible associations of oxide forms of trace and minor elements with the major igneous and pegmatitic rock forming elements.

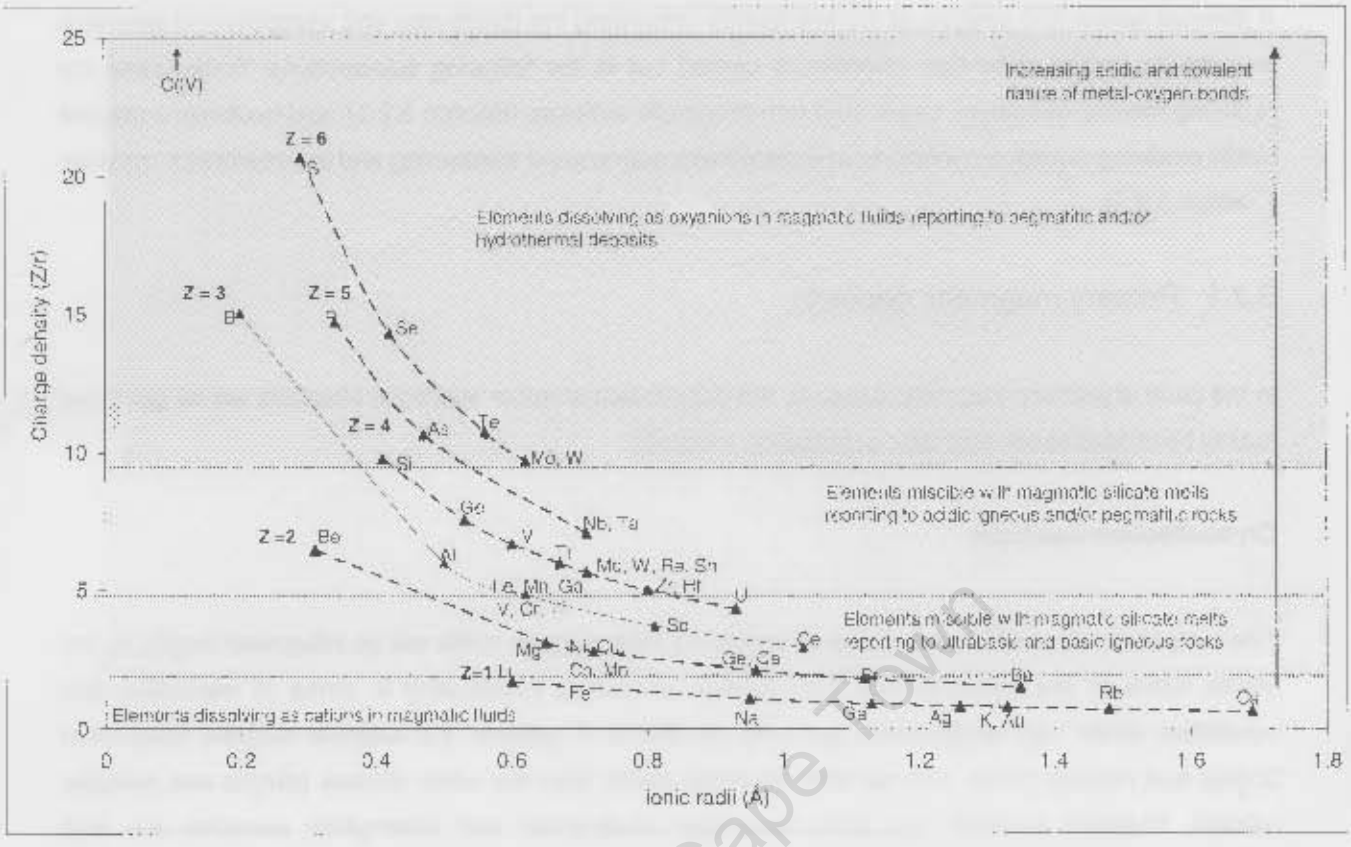


Figure 3.6: Ionic radii and charge densities as a function of their oxidation state (ionic radii sourced from Kneen et al. 1972)

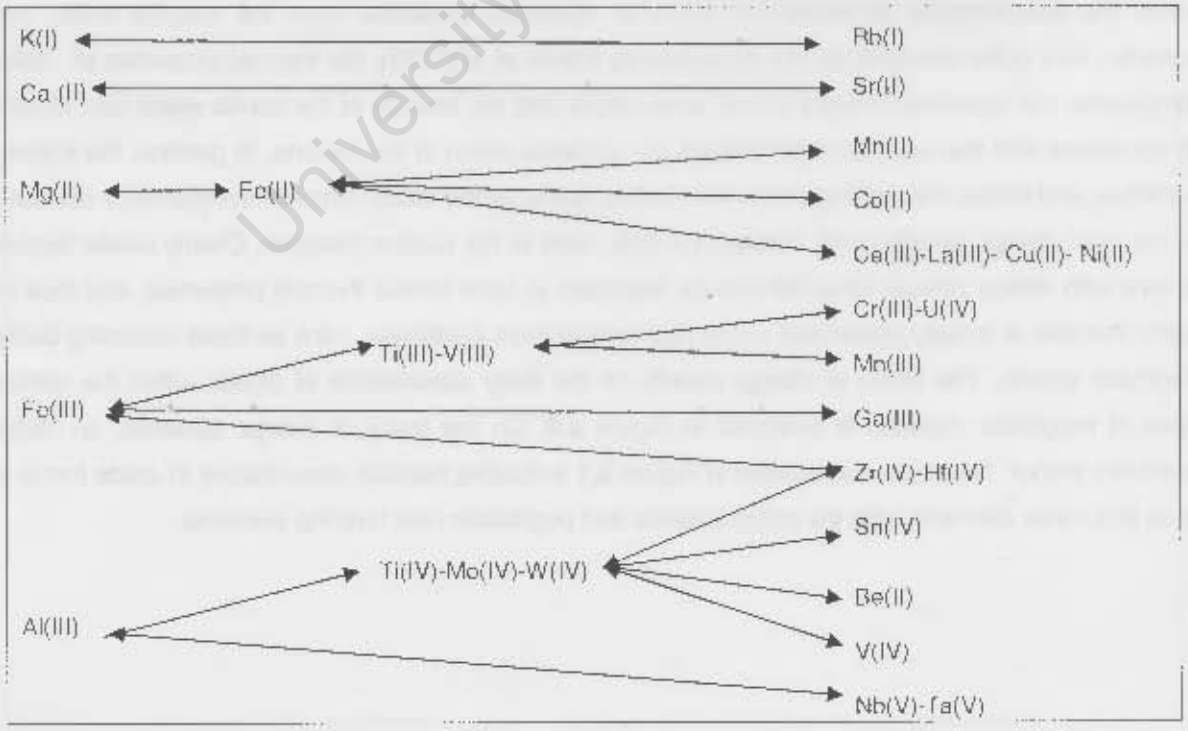


Figure 3.7: Oxide miscibility model for magmatic igneous and pegmatitic rock deposits

A number of lithophilic elements remain in the aqueous and/or or gas phase, along with the sulphide forming chalcophilic elements and siderophiles, at the high temperatures associated with the deposition of igneous rock deposits (ultra-basic to acidic rocks). Such elements include the divalent metal cations (particularly calcium, magnesium and barium) forming stable solid phases with oxyanions (mainly phosphate, carbonate, sulphate and borate); the simple oxides of the alkali metals and silica (quartz); as well as the volatile halides. These elements are transported in their stable forms within the hot residual magmatic solutions, gases and water vapour through rock fissures and cracks to the earth's surface, resulting in the gradual formation of hydrothermal mineral deposits on the walls of the fissures upon cooling. As indicated in Figure 3.2, hydrothermal deposits are generally divided into three temperature ranges, with the temperature of crystallisation decreasing on going from the hypothermal to the mesothermal to the epithermal range. Although the thermal stabilities and hence the melting and boiling points of the covalent sulphide compounds at elevated temperatures appear to be linked to the extent of metal-metal bonding or alloy-like character of the compounds, metal sulphides frequently have peculiar and complex stoichiometries, and are generally not well understood. Mineral associations commonly reported (see for example Batty, 1981; Correns, 1969; Duda & Rejl, 1986) for the various types of hydrothermal deposits are presented in Appendix 3.1. Figure 3.8 indicates potential associations of selected hydrothermal minerals on the basis of their melting and sublimation temperatures.

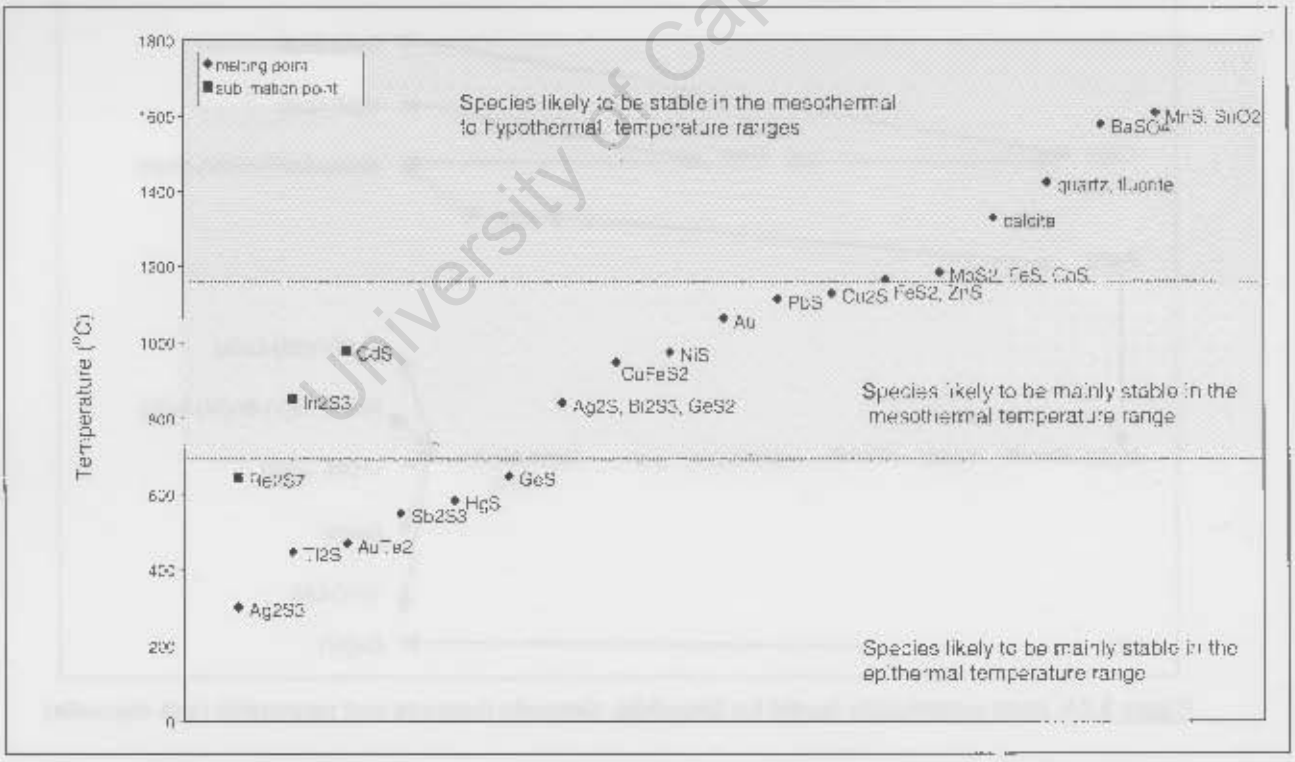


Figure 3.8: Stable temperature ranges of hydrothermal minerals as a function of melting and sublimation points (melting and sublimation temperatures have been sourced from Elliot & Gleiser, 1997; Lide, 1997; Outokumpu, 2002)

Ionic substitution reactions

In many cases trace to minor elements occur as isomorphous associations dispersed within the mineral structures of the major elements, as opposed to discrete phases. Such isomorphous associations can be attributed largely to the similarity of size and properties of their atoms and ions with those of the more abundant elements, resulting in their replacement within the compound crystal structure. According to Thornton (1983) substitution can occur if the difference in ionic size is less than or equivalent to 15%. On this basis a model, termed an "ionic substitution model", has been constructed in Figure 3.9, providing an indication of the feasible isomorphic associations of trace and minor elements with major mineral-forming elements on the basis of their relative ionic radii. Many trace to minor elements, including Ga, Ge, In, Re, Tl, Rb and Hf, occur almost exclusively as dispersed elements, whilst the stable forms of iron and magnesium generally play host to a number of minor to trace elements. In particular pyrite, a major mineral in most sulphide deposits, frequently contains a number of isomorphous co-elements, including arsenic (up to 10 weight percent) and other elements such as cobalt (up to 3%), nickel (up to 10%), zinc and copper (Seal & Foley, 2002).

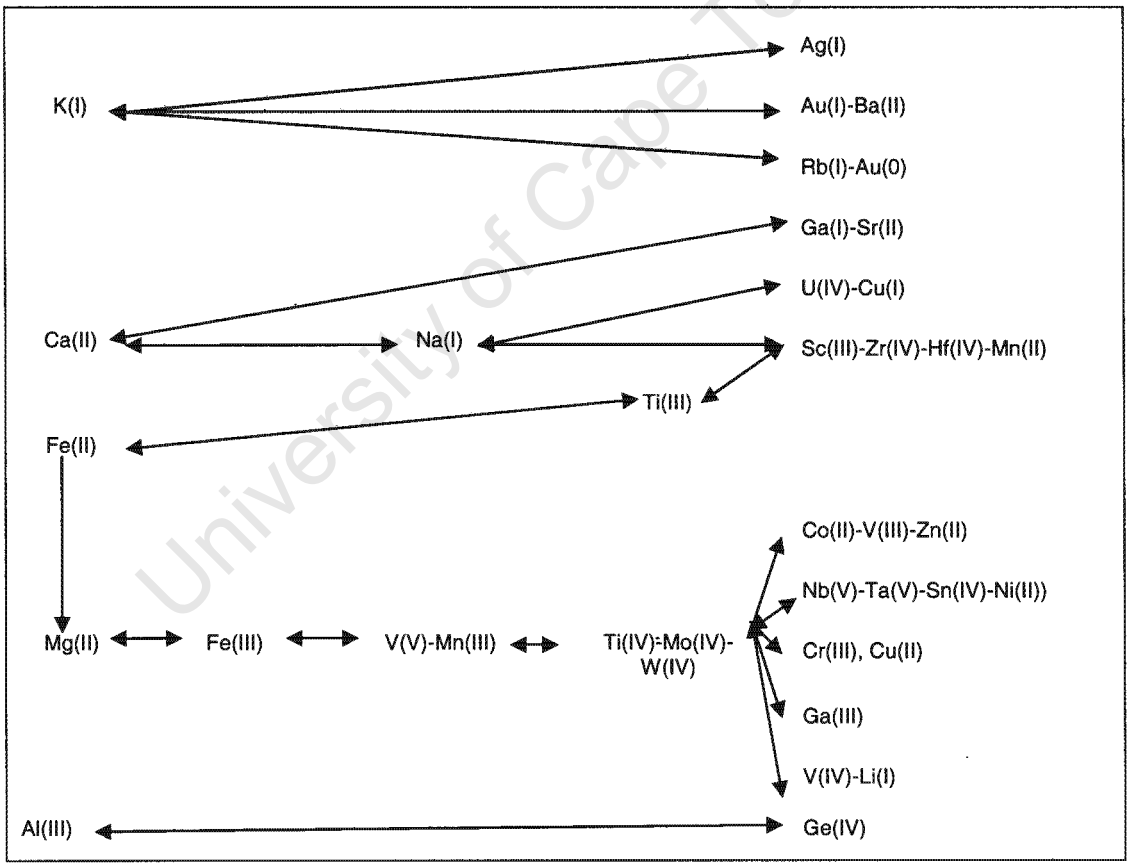


Figure 3.9A: Ionic substitution model for lithophilic elements (igneous and pegmatitic rock deposits)

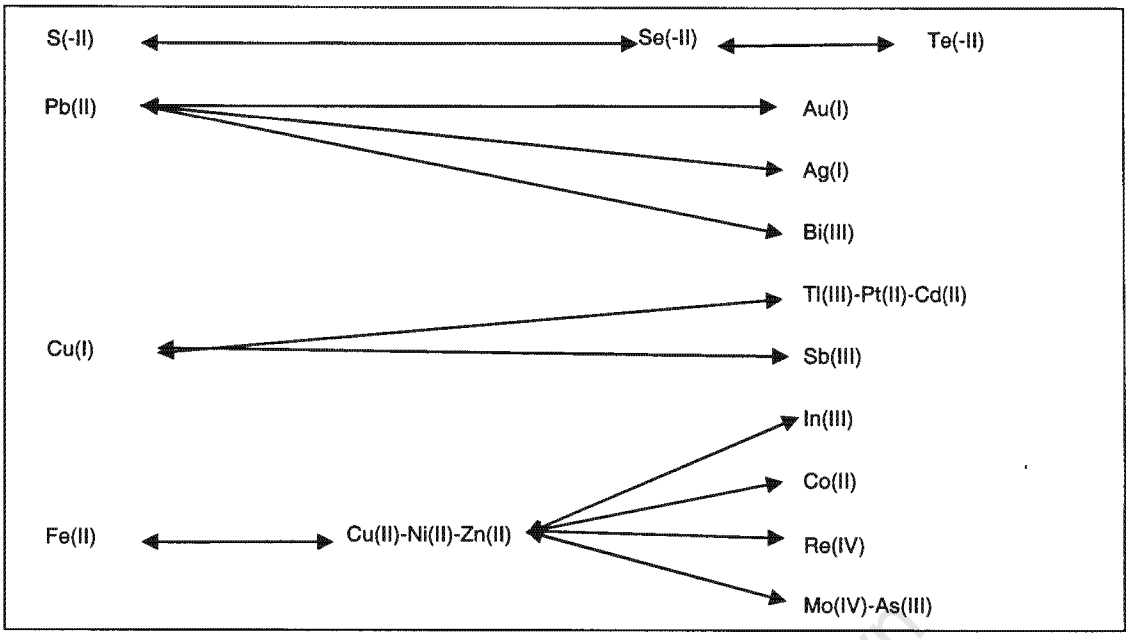


Figure 3.9B: Ionic substitution model for chalcophiles and siderophiles (hydrothermal sulphide deposits)

3.2.2 Sedimentary deposits

The magmatic deposits described in the previous section are not in equilibrium with conditions at the earth's surface and are thus eroded and chemically altered by weathering and sedimentation, as indicated in the general flowsheet in Figure 3.10. During chemical weathering, the minerals in magmatic deposits are changed into phases which are stable under conditions of ambient temperatures and pressures, through chemical weathering by air and water. Physical weathering breaks the rocks into smaller fragments, increasing the surface area exposed to these chemical agents, and thus enhancing the rate of chemical weathering.

In contrast to primary magmatic deposits, the deportment of elements to, and compositions of, sedimentary deposits (which include shales, limestone, sandstone, laterites, evaporites and coal) will be governed by a number of reaction mechanisms and influencing parameters relating to the local geology, hydrology and climatology. Considerable variations in the compositions (in terms of both the major and minor/trace minerals) of sedimentary deposits may thus occur as a result of changes in the physical and chemical conditions during weathering, transportation and deposition. Despite these complexities, the weathering of magmatic deposits is essentially a process entailing separation of attenuated and unattenuated elements, and can thus be largely considered within the framework of relative element mobilities under naturally occurring conditions. As in the case of solid mineral waste constituents (see the chemical behaviour model and related discussions in Section 2.2), the chemical mobility of solid phases in magmatic deposits will be determined in the first place by the stability or reactivity of the primary mineral phases in the magmatic deposits as a function of local environmental conditions (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 dependent on a number of parameters, including constituent activity, redox potential, the nature and concentration of major soluble ions and the sedimentary deposits 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 relatively rapid weathering and mobilisation of associated elements, to slow kinetically-controlled reactions, which are only likely to result in significant weathering in the medium- to long-term.

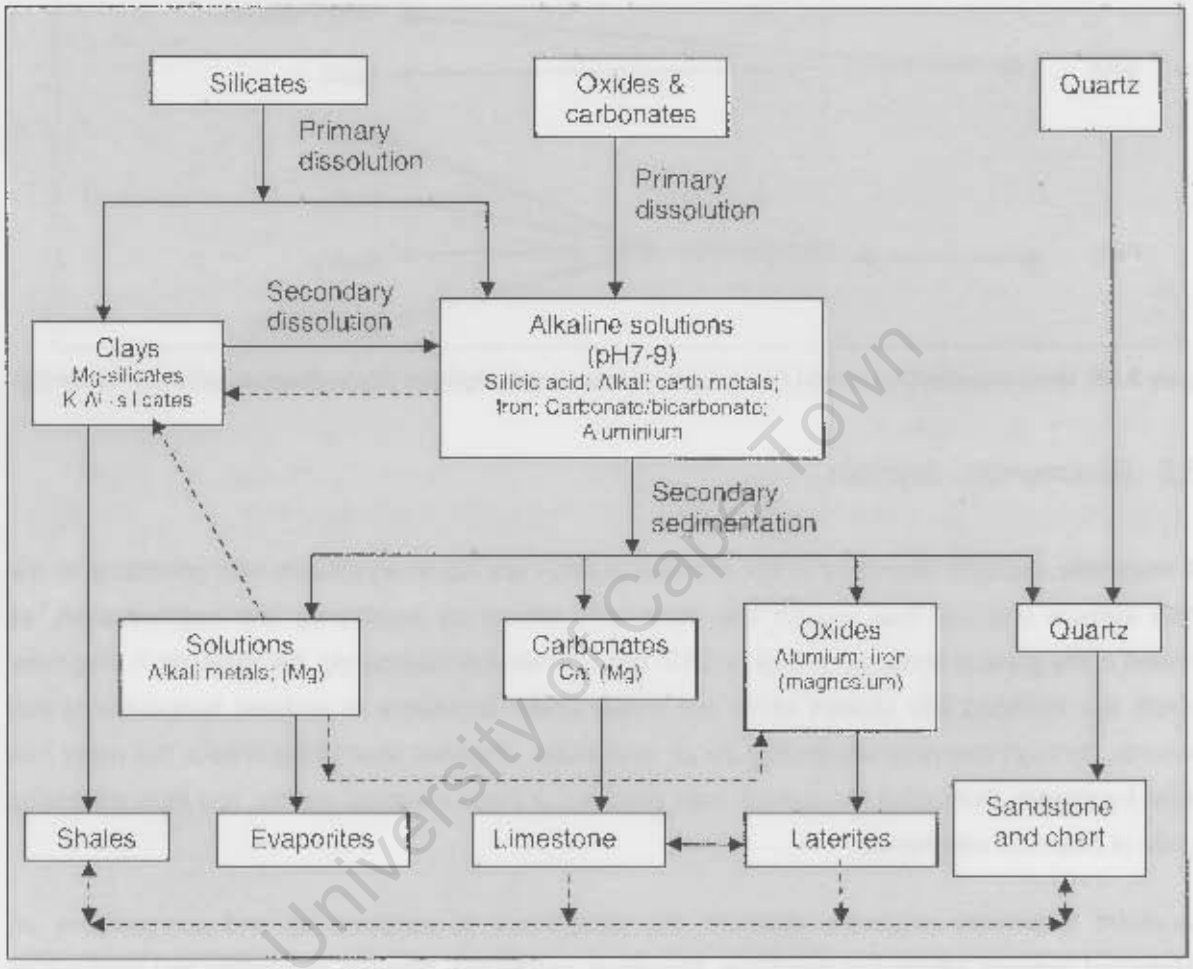


Figure 3.10: Generalised flowsheet for the formation of sedimentary deposits

Typical weathering and sedimentation reactions of the common major minerals in naturally-occurring deposits are presented in Appendix 3.2. The corresponding distributions of minor and trace elements can, in turn, be predicted from a knowledge of the Eh-pH regions of dominance for their stable forms, as presented for example by the Eh-pH diagrams of Brookins, 1988. As indicated in the reactivity model in Table 3.4, this allows elements to be grouped in accordance with their chemical behaviour patterns, and hence likely associations in sedimentary or weathered primary deposits, as a function of natural redox potential and pH conditions.

Table 3.4: Eh-pH reactivity model

Element description	Conditions of reaction		Reaction products
	pH	Redox potential	
Group1: elements forming stable oxides or metals (unreactive under most natural pH and redox conditions)			
IA: oxides			
Zr(IV)-Hf(IV)-Ti(IV)	None	None	None
Sn(IV)	None	None	None
Nb(V)-Ta(V)	None	None	None
Sb(V)	None	None	None
IB: metals			
Au	None	None	None
Ag	Acidic-alkaline	Oxidising	Ag(I) cation
Hg*-PGMs	Acidic (<4) Neutral-alkaline	Oxidising Oxidising	Cations Oxides/ oxyanions
Se-Te	Acidic-alkaline	Oxidising	Se(IV)-Te(IV) oxyanions
Group 2: elements forming moderately stable oxides (partially reactive under specific conditions)			
In(III)*-Bi(III)*	Acidic (<5)	Transitional-oxidising	Cations
Fe(III)-Mn(III)	Acidic Neutral	Transitional-oxidising Transitional	Cations Cations
Cr(III)-V(III)/(IV)	Acidic Neutral-alkaline	Transitional-oxidising Oxidising	Cations Oxyanions
Tl(III)	Acidic-alkaline	Transitional	Tl(I) oxides and cations
Be(II)-Al(III)- Ga(III)-Sc(III)	Acidic (<4) Alkaline (>10)	Transitional-oxidising Transitional-oxidising	Cations Oxyanions
Si(IV)-Ge(IV)	Alkaline (>12)	Transitional-oxidising	Oxyanions
Re(IV)*-Mo(IV)*-W(IV)	Acidic-alkaline	Transitional-oxidising	Re(VI)-Mo(VI)-W(VI) oxides and oxyanions
Ti(III)	Acidic-alkaline	Transitional-oxidising	Ti(IV) oxides
Group 3: elements forming moderately unstable oxides (relatively reactive under a wide range of conditions)			
Ni(II)-Co(II)	Acidic-neutral (<8) Highly alkaline (>12)	Transitional-oxidising Transitional-oxidising	Cations Oxyanions
Cd(II)*-Zn(II)*-Mg(II)	Acidic-neutral (<6-8) Alkaline (8-10) Highly alkaline (>12)	Transitional-oxidising Transitional-oxidising Transitional-oxidising	Cations Partial carbonate formation Oxyanions
Cu(II)*	Acidic (<6-8) Neutral -Alkaline	Transitional-oxidising Transitional	Cations Metal
Fe(II)*-Mn(II)	Acidic Neutral-alkaline Neutral-alkaline	Transitional-oxidising Transitional Oxidising zone	Cations Fe(III)-Mn(III) oxides and/or Fe(II)-Mn(II) carbonates Fe(III)-Mn(III) oxides
Tl(I)*	Acidic-alkaline Acidic-alkaline	Transitional Oxidising	Tl(I) cations Tl(III) oxide
Ca(II)-Sr(II)-Pb(II)*	Strongly acidic (<4) Acidic-neutral Neutral-alkaline	Transitional-oxidising Transitional-oxidising Transitional-oxidising	Cations Sulphates Carbonates
Ba(II)	Acidic-alkaline	Transitional-oxidising	Sulphate
Group 4: Elements forming unstable oxides (reactive under most natural conditions)			
Alkali metals	Acidic-alkaline	Transitional-oxidising	Cations
B(III)-P(V)-As(V)-S(VI)	Acidic-alkaline	Transitional-oxidising	Oxyanions
Re(VII)-Mo(VI)-W(VI)	Acidic-alkaline	Transitional-oxidising	Oxyanions
As(III)-Sb(III)	Acidic-alkaline	Transitional-oxidising	As(V)-Sb(V) oxides

*elements form stable sulphide minerals under non-oxidising (reducing) conditions

3.3 Summary and concluding remarks

As all solid wastes produced by the mineral-based resource industries originate from naturally occurring mineral deposits, addressing current data gaps and inconsistencies pertaining to the chemical compositions of such deposits, particularly in terms of trace to minor elements, is a prerequisite to the reliable prediction of the key characteristics of solid mineral wastes on the basis of their origins and source.

The specific aim of this chapter was to develop a fundamental understanding of the key mechanisms and parameters controlling the distribution behaviour of elements, and groups thereof, within naturally occurring mineral deposits. This was done by combining the fundamental principles of mineralogy, geochemistry, as well as basic inorganic chemistry. On this basis, key criteria for estimating element distribution behaviour during formation of ore deposits have been identified, and models for predicting element associations as a function of these criteria established. The key qualitative information generated through this study, in terms of addressing data gaps and inconsistencies pertaining to the chemical compositions of ore deposits, is summarised in Figure 3.11.

Methodological guidelines for the practical application of this information in predicting element enrichment factors and concentrations within feed ores (and other mineral resource-based industry operation streams) are provided in Chapter 5. Such application is subsequently demonstrated for the case of porphyry-type copper sulphide ores within Chapter 6.

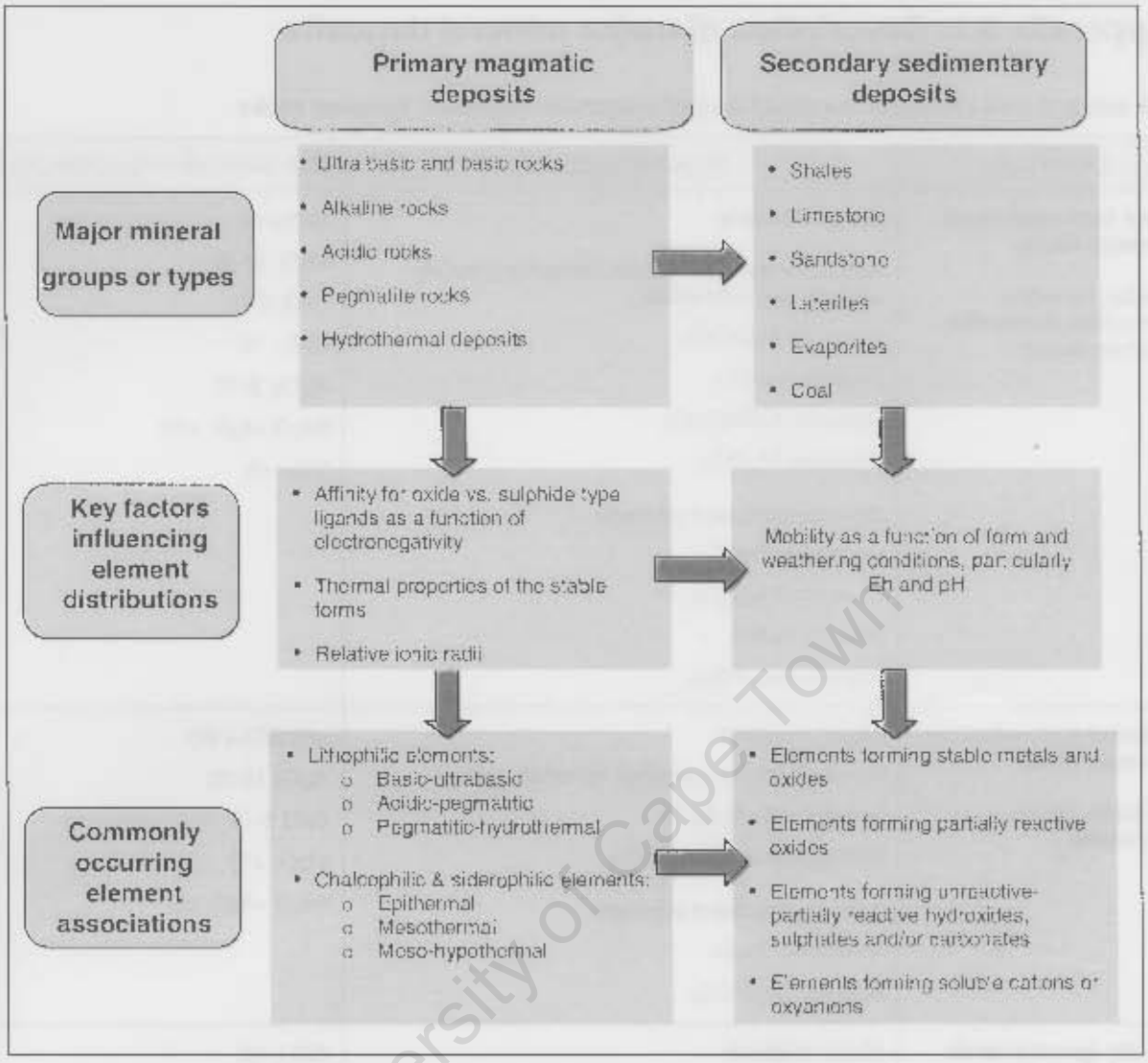


Figure 3.11: Summary of element distribution behaviour and associations within mineral deposits

Appendix 3.1: Description of major mineral deposits

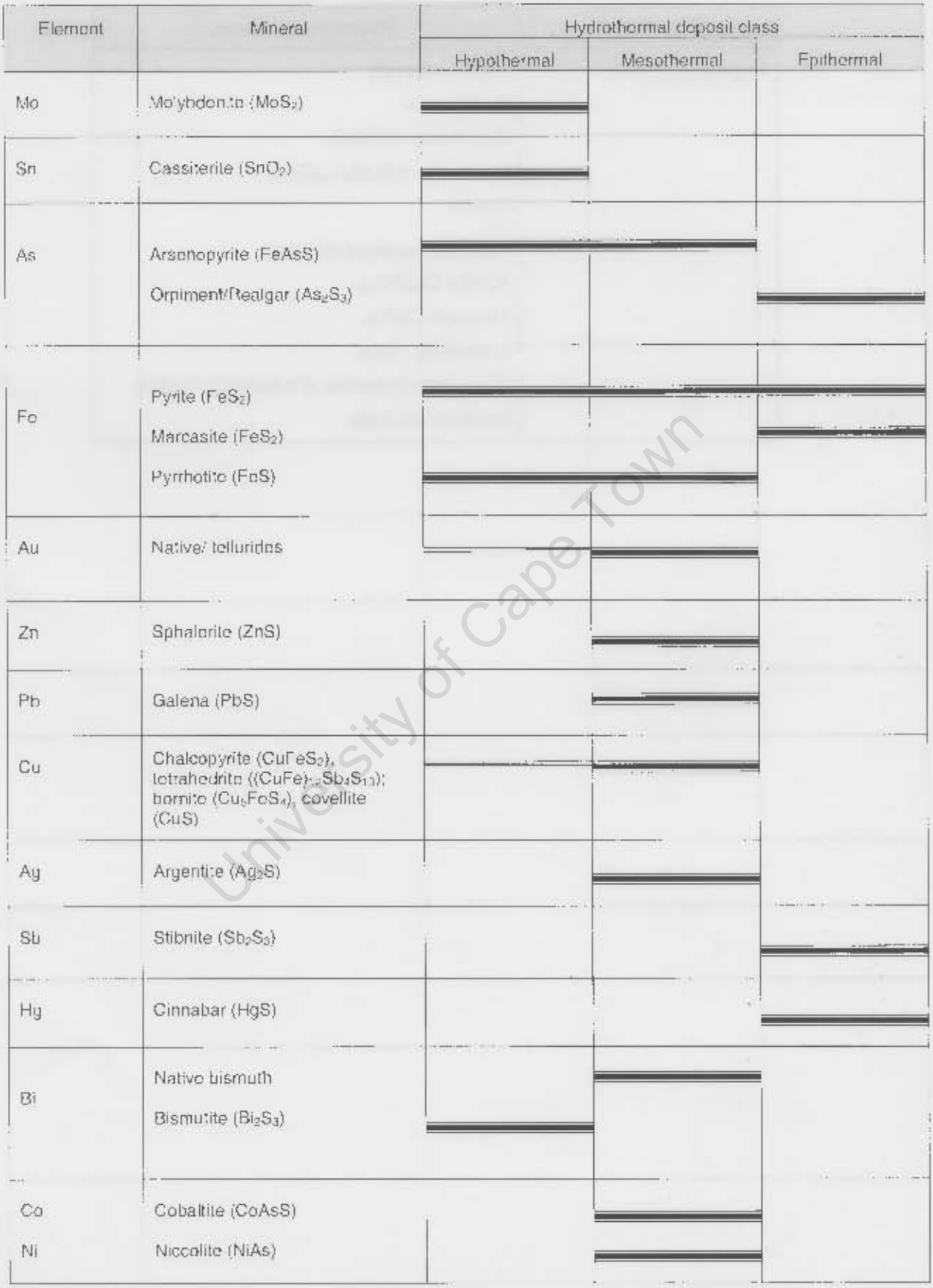
Bulk mineral and chemical compositions of magmatic deposits: Igneous rocks

Deposit type	Mineral compositions	Bulk chemical composition (%)
Ultra basic and basic igneous rocks: Dunite, Periodite, Pyroxenite, Kimberlite, Gabbro, Basalt	***Major minerals*** Mg and/or iron rich silicate, comprising mainly olivine's and pyroxenes: Fosterite: Mg_2SiO_4 Fayalite: Fe_2SiO_4 Diopside: $CaMgSi_2O_6$ Enstatite: $MgSiO_3$ ***Minor/associated minerals*** Magnetite: Fe_3O_4 Chromite: $FeCr_2O_4$ Ilmenite $FeTiO_3$ Apatitie: $Ca_5(PO_4)_3$	SiO_2< 50 MgO: 10-50 FeO: 5-10 CaO: 10 Al_2O_3: 2-12 $Na_2O + K_2O$: <10 TiO_2: <3
Alkaline (calc-alkaline) igneous rocks Andesite, Diorite, Monzanite	***Major minerals*** Mainly Ca-rich plagioclase minerals such as Anorthite: $CaAl_2Si_2O_8$ Stilbite: $CaNa_2K_2Al_2Si_{17}O_{18}$ ***Minor/associated minerals*** Magnetite: Fe_3O_4 Apatitie: $Ca_5(PO_4)_3$	<50 SiO_2< 60 Al_2O_3 15-20 CaO 5-15 MgO: <10 $Na_2O + K_2O$: <5
Acidic igneous rocks Granite, Rhyolite	***Major minerals*** Alkali and Al rich silicates: K and Na -feldspars: Albite: $NaAlSiO_3$ Orthoclase: $KAlSi_3O_8$ Quartz (SiO_2) ***Minor/associated minerals*** Magnetite: Fe_3O_4 Apatitie: $Ca_5(PO_4)_3$ Zircon: $ZrSiO_4$ Sphene: $CaTi(SiO_4)$	SiO_2> 60 Al_2O_3 :15 $Na_2O + K_2O$: 10 CaO <5 MgO <1 FeO< 5

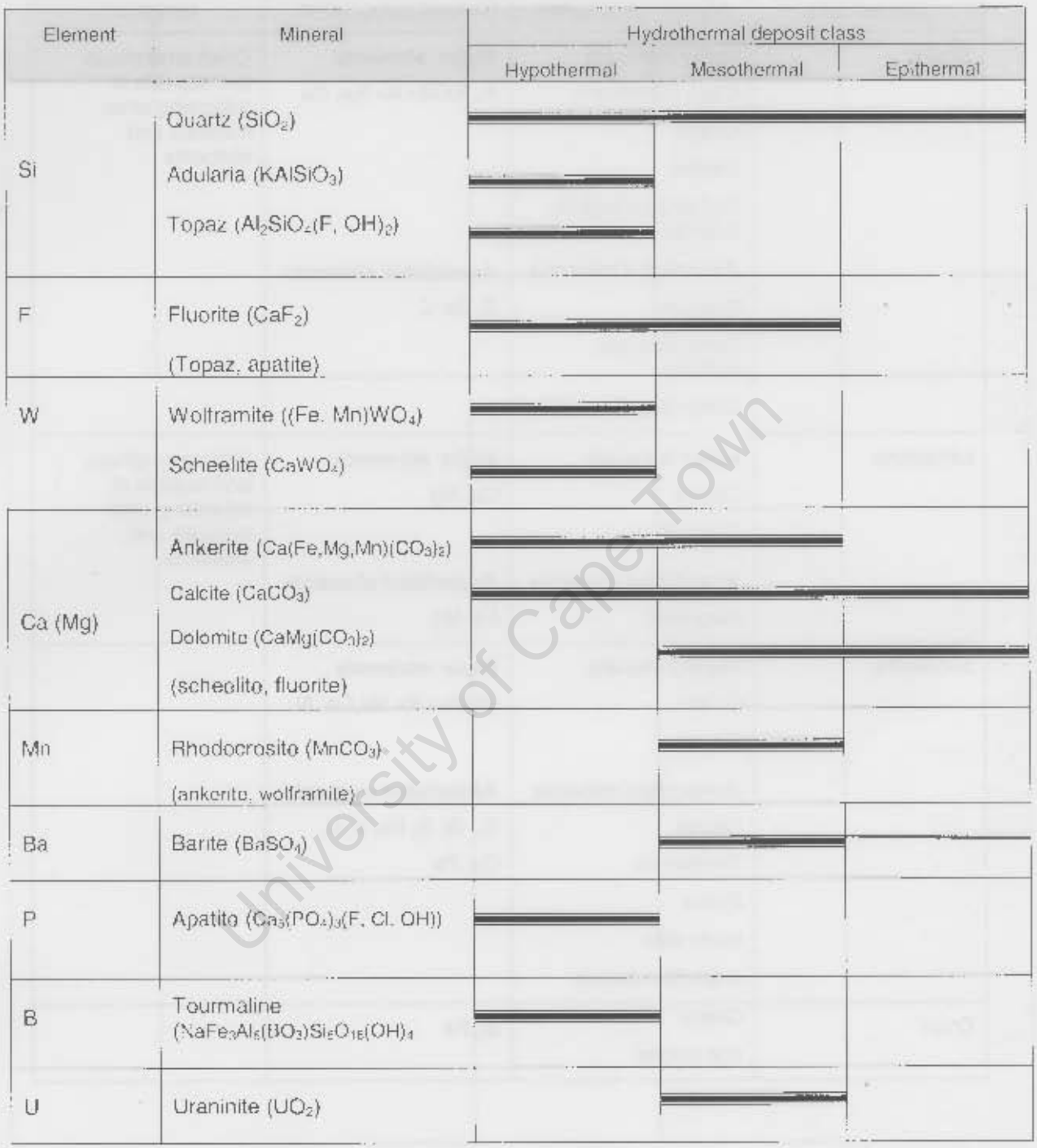
Bulk mineral and chemical compositions of magmatic deposits: Pegmatite rocks

Deposit type	Mineral compositions
Pegmatite deposits	***Major minerals*** K-feldspars: Orthoclase: $KAlSi_3O_8$ Muscovite: $KAl_3Si_3O_{10}(OH)_2$ Quartz ***Minor/associated minerals*** Apatite $Ca_5(PO_4)_3$ Monazite $CePO_4$ Cassiterite: SnO_2 Wolframite/Scheelite: $(Fe,Mn)WO_4/CaWO_4$ Molybdenite: MoS_2

Mineral associations of hydrothermal deposits



Mineral associations of hydrothermal deposits continued....



Sedimentary deposits and their bulk chemical compositions

Deposit type	Mineral composition	Element composition	comments
Shales	***Major minerals***	***Major elements***	Often amorphous and capable of adsorbing other minerals and elements
	Clays (dominant)	Al, SiO2> K> Na, Ca	
	Quartz		
	Oxides		
	Carbonates (calcite, siderite)		
	Associated minerals	***Associated elements***	
	Gypsum	S, Ba, C	
	Carbonaceous material		
	Barite (BaSO4)		
Limestone	***Major minerals***	***Major elements***	Often amorphous and capable of adsorbing other minerals and elements
	Calcite	Ca, Mg	
	Dolomite		
	Associated minerals	***Associated elements***	
	Magnetite	Fe, Mn	
Sandstone	***Major minerals***	***Major elements***	
	Quartz	SiO2>> K> Na,Ca, Al	
	Clays		
	Associated minerals	***Associated elements***	
	Calcite	Ti, Zr, B, Fe, V, U,	
	Ti-minerals	Cu, Pb	
	Zircon		
	tourmaline		
	sulphide minerals		
Chert	Quartz	Si, Fe	
	Iron oxides		

Sedimentary deposits and their bulk chemical compositions continued.....

Deposit type	Mineral composition	Element composition	comments
Oxides: Fe Laterites	 Hematite Goethite	 Fe	Often amorphous and capable of adsorbing other minerals and elements
Aluminium Bauxites	Gibbsite Bohemite Diaspore	Al	
Manganese oxides		Mn	
Evaporites	Halite Sulphates Dolomite Phosphates	Na, Cl, Ca, K	
Soils	Clays Quartz Organic materials	Al, Si, alkaline earth metals	

Appendix 3.2: Typical reactions involved in the weathering and sedimentation of bulk mineral compounds

Primary weathering reactions

Acid hydrolysis (neutralising reactions)
Silicate minerals
$5Mg_2SiO_4 + 2H_2O + 8H^+ \rightarrow 2Mg_3(OH)_4Si_2O_5 + H_4SiO_4 + 4Mg^{2+}$ *Forsterite* *Serpentine*
$4Mg_2SiO_4 + 8H^+ + CO_2 \rightarrow Mg_3(OH)_2(Si_4O_{10}) + 5Mg^{2+} + 3H_2O + CO_3^{2-}$ *Forsterite* *Talc*
$Fe_2SiO_4 + 4H^+ \rightarrow 2Fe^{2+} + H_4SiO_4$ *Fayalite*
$2KAlSi_3O_8 + 9H_2O + 2H^+ \rightarrow 2K^+ + Al_2Si_2O_5(OH)_4 + 4H_4SiO_4$ *K-feldspar* *Kaolinite*
$3KAlSi_3O_8 + CO_2 + 13H_2O \rightarrow 2K^+ + KAl_3Si_3O_{10}(OH)_2 + 6H_4SiO_4 + CO_3^{2-}$ *K-feldspar* *Muscovite*
$KMg_{1.5}Fe_{1.5}AlSi_3O_{10}(OH)_2 + 10H^+ \rightarrow K^+ + Al^{3+} + \frac{3}{2}Mg^{2+} + \frac{3}{2}Fe^{2+} + 3H_4SiO_4$ *Biotite*
$NaAlSi_3O_8 + 4H_2O + 4H^+ \rightarrow Na^+ + Al^{3+} + 3H_4SiO_4$ *Albite*
$CaAl_2Si_2O_8 + 8H^+ \rightarrow Ca^{2+} + 2Al^{3+} + 3H_4SiO_4$ *Anorthite*
Carbonate minerals *(6.5 < pH < 10)*
$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$ *Calcite*
$(CaMg)_{0.5}CO_3 + H^+ \rightarrow 0.5Ca^{2+} + 0.5Mg^{2+} + HCO_3^-$ *Dolomite*
$FeCO_3 + H^+ \rightarrow Fe^{2+} + HCO_3^-$ *Siderite*
$(CaFe)_{0.5}CO_3 + H^+ \rightarrow 0.5Ca^{2+} + 0.5Fe^{2+} + HCO_3^-$ *Ankerite*
Oxides
$CaO + 2H^+ \leftrightarrow Ca^{2+} + H_2O$ *Lime*
$Fe_3O_4 + 8H^+ \rightarrow Fe^{2+} + 2Fe^{3+} + 4H_2O$ *Magnetite*
$Fe_2O_3 + 6H^+ \rightarrow 2Fe^{3+} + 3H_2O$ *Haematite*

Primary weathering reactions continued.....

Acid generating reactions
Oxidative dissolution of sulphide minerals
$FeS_2 + 3.5O_2 + H_2O \leftrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$ *Pyrite*
Carbon dioxide dissolution and dissociation
$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$

Secondary weathering reactions:

Acid hydrolysis (neutralising reactions)
$Mg_3(OH)_4Si_2O_5 + 5H^+ \rightarrow 3Mg^{2+} + 2H_4SiO_4 + OH^-$ *Serpentine*
$Mg_3(OH)_2(Si_4O_{10}) + 4H_2O + 6H^+ \rightarrow 3Mg^{2+} + 4H_4SiO_4$ *Talc*
$Al_2Si_2O_5(OH)_4 + 5H^+ \rightarrow 2Al^{3+} + 2H_4SiO_4 + OH^-$ *Kaolinite*
$KAl_2[AlSi_3O_{10}](OH)_2 + 10H^+ \rightarrow K^+ + 3Al^{3+} + 3H_4SiO_4$ *Muscovite*
Oxidation reactions
$2Fe^{2+} + 0.5O_2 + 2H^+ \leftrightarrow 2Fe^{3+} + H_2O$

Secondary sedimentation reactions

Sedimentation Reactions
$H_4SiO_4 \rightarrow SiO_2 + 2\ H_2O$ *Quartz*
$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3H^+$ *Fe(III) hydroxides and oxyhydroxides (goethite, haematite)*
$Al^{3+} + 3OH^- \rightarrow Al(OH)_3$ *Al(IIII) hydroxides and oxyhydroxides (gibbsite/bohemite)*
$M^{2+} + OH^- \rightarrow M(OH)_2$ *Divalent metal hydroxides and oxyhydroxides (Ca, Mn)*
$M^{2+} + CO_3^{2-} \rightarrow MCO_3$ *Divalent metal carbonates (Ca, Mg, Fe, Mn)*
$M^{2+} + SO_4^{2-} \rightarrow MSO_4$ *Divalent metal sulphates (Ca, Ba)*

"...if the dynamics of metallurgical reactors are not understood, sustainability at a bigger scale remains a myth" Reuter et al, 2003

4

The Beneficiation of Ores: Establishing the Primary Source of Solid Mineral Wastes

Due to the complex nature of ore bodies, systems for the primary processing of mineral resources and the associated material flows are themselves inherently complex, and generally comprised of multiple processing stages, each with a number of possible unit operations and output streams (see Figure 4.1).

As the targeted metal in any ore deposit is present in relatively small quantities, co-existent with a number of other constituents, the non-product outputs from the primary mineral-based resource industries are generally voluminous, with extremely variable and complex compositions. For any specific ore body (feed material), the distribution of ore components, and hence the compositions of each waste output stream, will be profoundly and directly influenced by the individual unit process operations, each of which is dictated by a set of conditions relating to technological performance on a reactor level. Apart from chemical compositions, the techniques and associated operating parameters employed for the extraction and beneficiation of ore deposits will also have an influence on other key waste characteristics, such as particle size, porosity and moisture content.

The mining and primary beneficiation of mineral resources, and in some cases the environmental aspects thereof, has been reviewed by a number of authors (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; Weis, 1985; Wills, 1997). These reviews affirm that the processing routes and technologies, and by implication the characteristics and quantities of waste outputs, will vary according to the characteristics of the ore deposit. Characteristics of particular relevance include grade, mode of occurrence (form and distribution) and grain size of the valuable or targeted constituents, as well as the nature of major impurities from which the valuables must be separated.

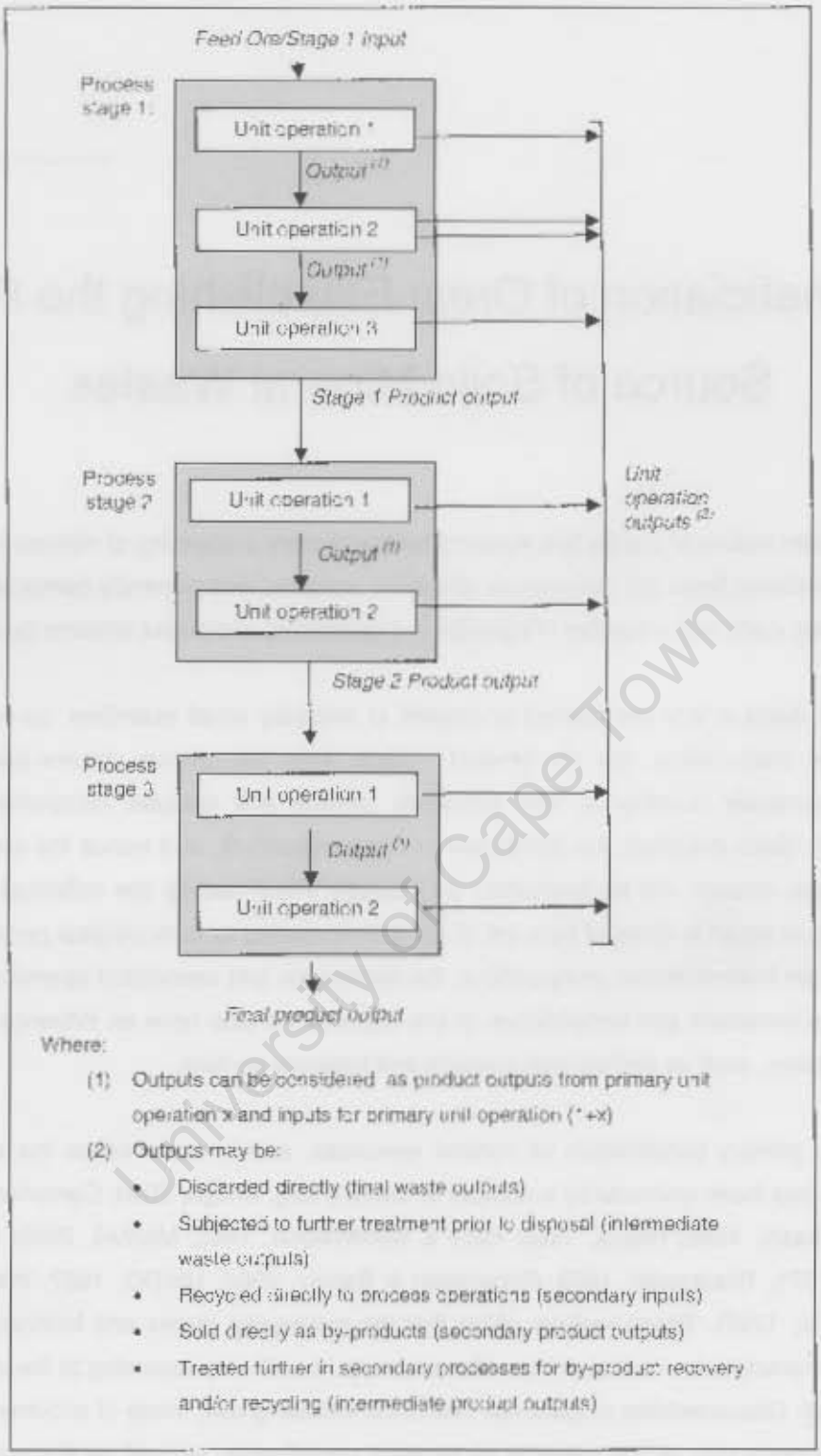


Figure 4.1: Generalised flowsheet for the primary processing of mineral resources

Despite the complex and varied nature of primary resource extraction and beneficiation processes and related input/output streams, the solid wastes arising from the mining and primary beneficiation of mineral resources can be grouped into a number of generic waste types or classes, with each class or type of waste being linked to specific processing stages and/or associated technologies, typical of the industry (see Figure 4.2).

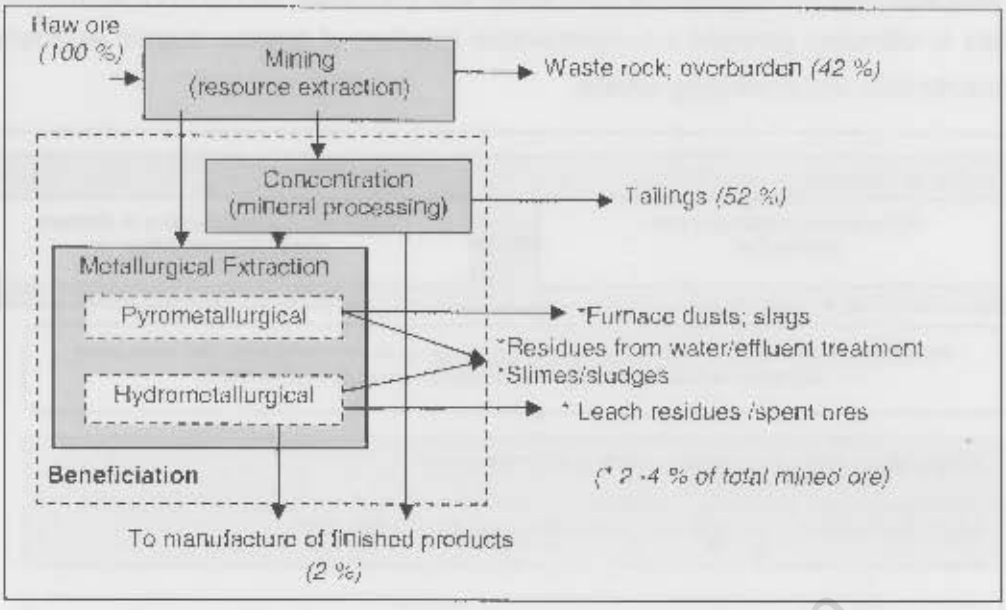


Figure 4.2: Typical mining and beneficiation flowsheet for the primary metal resource industry

According to average industry figures reported by Warhurst (2000), 42% of the total mined material is typically rejected in the form of waste rock during mining; a further 52% is discarded in the form of tailings during concentration of the run-of-mine ore; whilst metallurgical extraction typically results in the rejection of an additional 4% in the form of various solid waste types (furnace slags, flue dusts, leach residues and/or effluent and wastewater treatment sludges). Whilst the share of the ore recovered as product will vary with grade, on average the valuable components typically account for only 2% of the original mined tonnage.

Due to their relevance in terms of technical and economic criteria, such as product quality and operational throughput, the distribution behaviour of the targeted metal and major ore components during extraction and subsequent beneficiation is generally fairly well understood, and indeed in the process of being normed into metal accounting systems (see current studies by Deglon & Chakraborty, 2006). 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, the reaction mechanisms and parameters controlling the distribution of minor and trace elements during processing are generally less well understood. Addressing data gaps and deficiencies in terms of these ore components will thus require reliable predictions of their distributions, based on a fundamental understanding of their chemical behaviour within reactor units. It is this understanding that this chapter of the thesis aims to address, by means of a fundamental assessment of the relationship between processing technologies, particularly in terms of the reactor variables and operating parameters, and the characteristics of the waste for each of the various processing stages in the ore-to-metal value chain (Sections 4.1 - 4.3).

Figure 4.3 illustrates how the fundamental information and knowledge can be reconciled with available empirical data to ultimately generate a comprehensive inventory of process outputs as a function of feed ore characteristics and processing options.

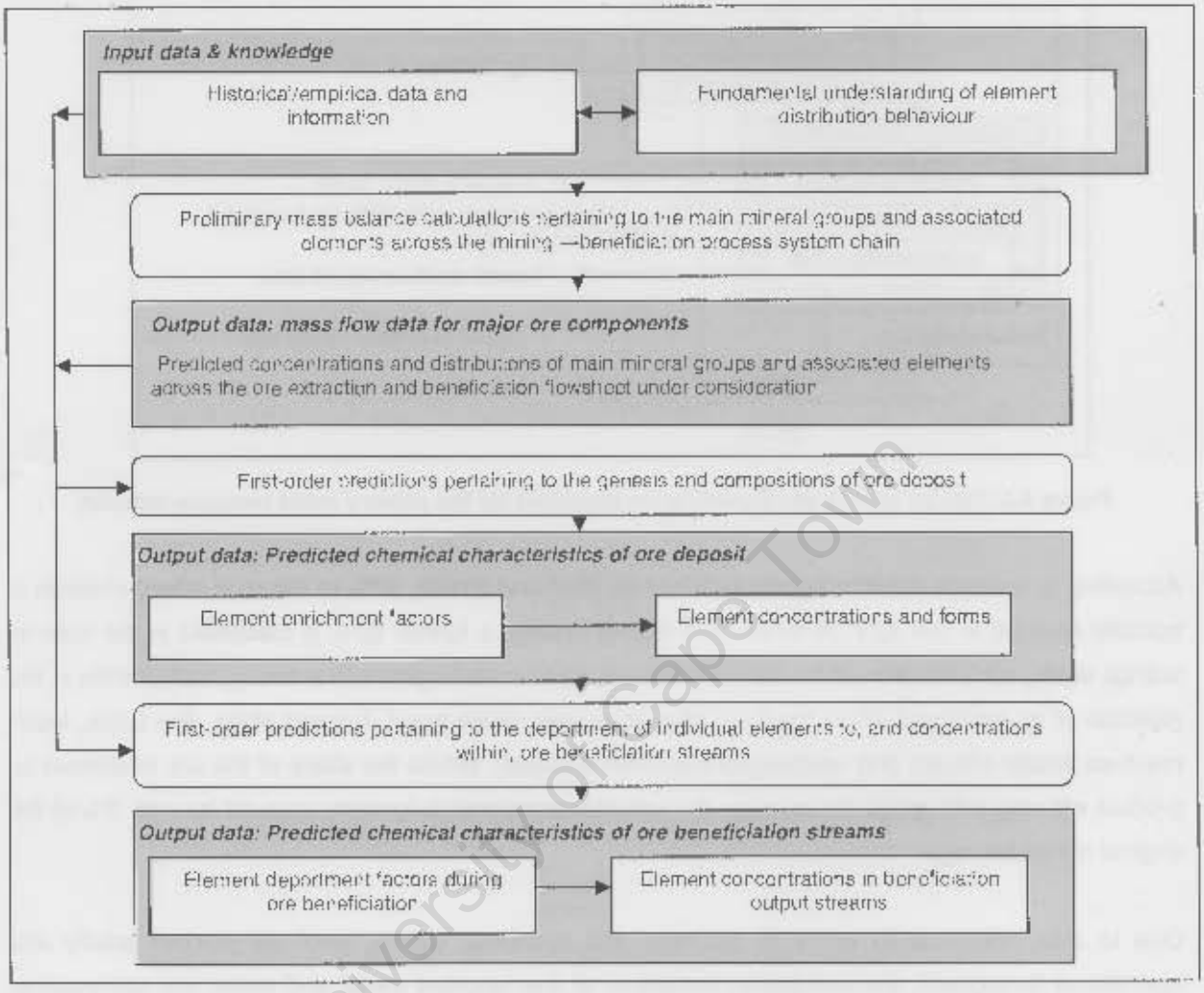


Figure 4.3: Generic procedural framework for predicting the chemical characteristics of ore deposits and beneficiation streams

Guidelines for the selection and application of the actual scientific techniques and methods for predicting element distribution and concentration data are provided within Chapter 5 of the thesis. Practical application in the case of the early beneficiation (extraction → concentration → smelting) of typical porphyry-type copper sulphide ores is demonstrated in Chapters 7 and 8.

4.1 Mining operations

Mining, or the process of raw ore extraction, forms the first processing stage in the commercial exploitation of all primary mineral resources, and can be defined as the act of separating the valuable mineral-bearing ore body from the host rock through physical extraction and crushing. In broad terms there are three types of mining (mining technologies), viz. surface mining (including open pit, open cast, strip and alluvial mining), underground mining and solution mining. Solution mining, which involves

injection of a suitable leaching agent into a porous, permeable mineral deposit, is relatively limited in application, though its extension into heap leaching is growing in significance as an integrated mining/beneficiation technology.

In order to gain access to the ore, underground and, in particular, surface mining entails the removal of large quantities of material, commonly referred to as waste rock, mine waste or overburden. In reality the distinction between ore (commonly referred to as run-of-mine (ROM) ore) and waste rock or overburden is an economic one, with material containing less than the cut-off grades being considered as waste, and disposed of on a waste dump. According to Thornton (1983), and consistent with the figures quoted by Warhurst (2000), 1 ton of run-of-mine ore corresponds on average to 1 ton of waste rock. This figure can, however, vary quite substantially, with open pit mining of low- grade ores (for example copper porphyry deposits) resulting in waste rock/ run-of-mine ore mass ratios of almost 2/1.

Mining typically results in 90-95% recovery of the valuable or targeted element-bearing minerals, with waste rock comprising the majority of the host rock, as well as 5-10% of the valuable or targeted metal. The chemical and mineralogical compositions of the waste rock will thus be highly dependent on that of the ore deposit and, in particular, the host rock with which it is associated. In general waste rocks will be made up of crushed porous rocks comprised mainly of silicates, carbonates, oxides and/or sulphides of the major elements.

4.2 Concentration of ROM ores

In some cases the run-of-mine ore is suitable for direct marketing or for economic extraction of the valuable constituents by means of relatively inexpensive heap leach techniques. In the majority of cases, however, the run-of-mine ore needs to be separated further from the gangue in order to produce a product suitable for sale (in the case of industrial, non-metallic minerals) or further metallurgical processing (in the case of most metal-bearing minerals).

Concentration, which is also referred to as mineral processing or initial beneficiation, can be defined as the separation of mineral phases by physical means (i.e. through the use of processes that do not result in chemical changes to the mineral component of the ore). The primary objective of concentration processes is to separate the valuable commodity-bearing minerals from the non-valuable minerals, thereby producing a concentrate, which has a smaller volume but higher-grade than the ROM ore, and a large volume discard tailings stream containing the majority of the gangue (non-valuable) minerals. In the case of complex ores, physical processing techniques are frequently also used to separate valuable minerals from each other.

As illustrated in Figure 4.4, most mineral processing or concentration systems typically consist of three unit operations, viz. milling; followed by physical solid-solid separation of the liberated minerals; and finally dewatering for the recovery of water from both the concentrate and tailings outputs.

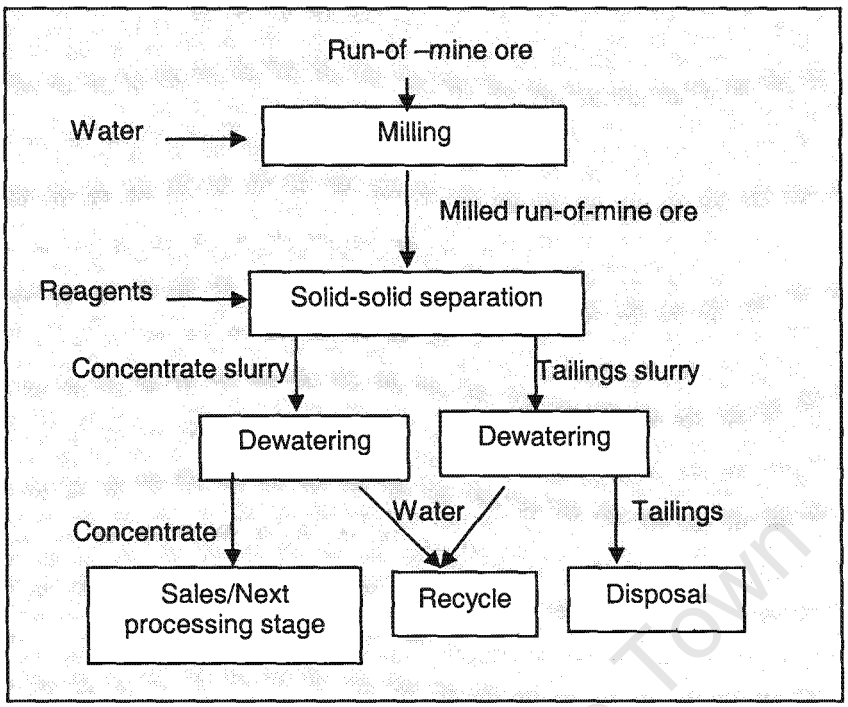


Figure 4.4: Hypothetical flowsheet of the concentration processing stage

4.2.1 Milling operations

The primary objective of milling (or comminution) is to reduce the size of the mineral particles so as to physically liberate the minerals from each other, prior to separation. The size at which adequate liberation is achieved will be dependent on the characteristics of the ore, and to a lesser extent on the physical separation processes. In the case of metallic mineral resources, particularly low-grade non-ferrous metal deposits, it is normally necessary to grind the ore relatively finely (<<1mm) in order to achieve acceptable recovery and concentration of the valuable constituents.

4.2.2 Solid-solid separation

Milling is generally followed by physical solid-solid separation of the liberated particles. A number of physical mineral processing or concentration methodologies and associated reactor technologies exist, the selection of which is mainly dependent on the physical and chemical differences between the minerals requiring separation. These technologies can be grouped according to their separation criteria, as indicated in Table 4.1. Figure 4.5 illustrates the particle size dependency of the commonly used concentration or mineral processing methods and technologies.

Table 4.1: Concentration methodologies and technologies as a function of solid-solid separation criteria

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

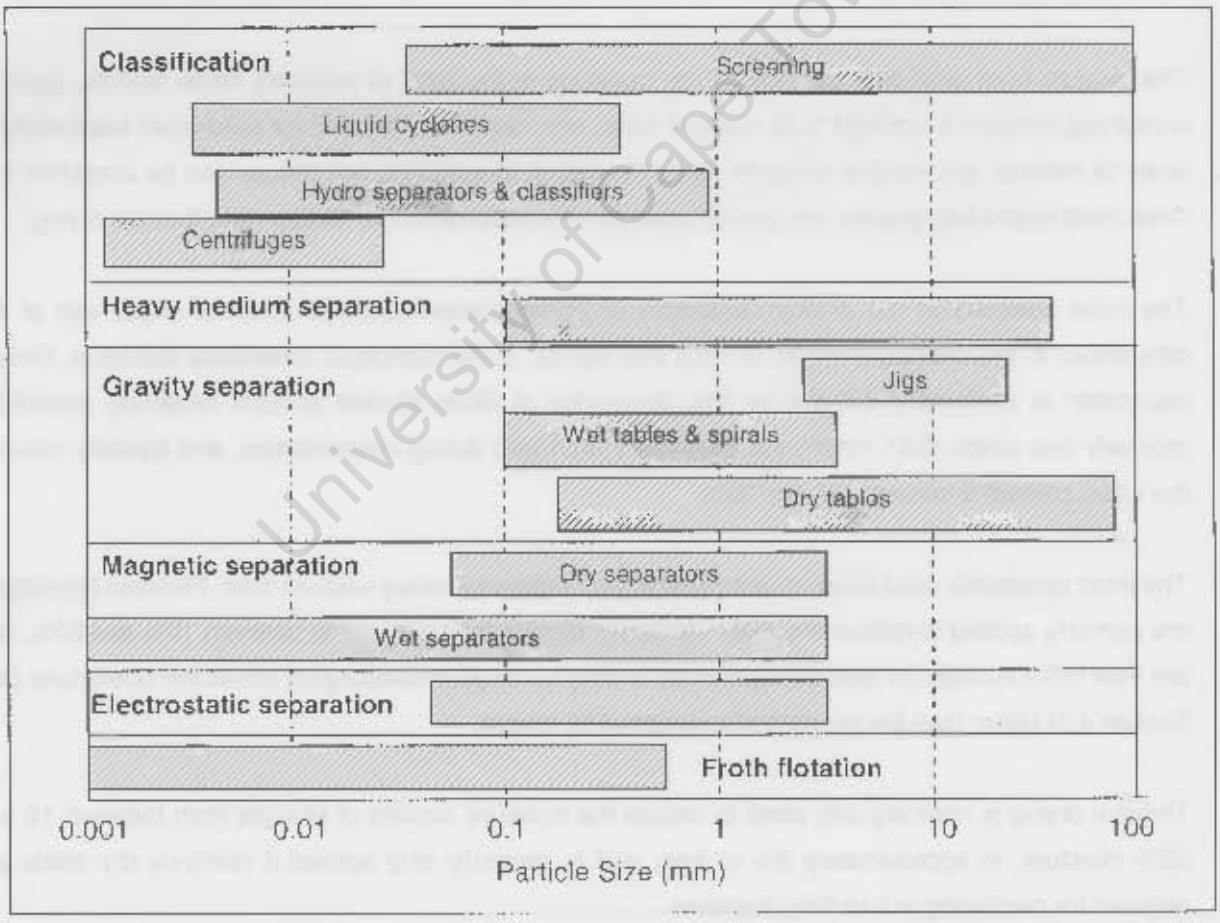


Figure 4.5: Particle size range for various concentration methodologies & technologies (Hayes, 1985; Roberts et al, 1971)

Because of the complexities of the ore mineralogy, no mineral separation process is fully effective in separating all feed particles into the desired products, even if they have been fully liberated by comminution ahead of separation. Whilst the efficiencies (in terms of recovery of the targeted

commodity) of the mineral processing operations are typically between 90 and 95%, Hayes (1985) reports that between 20 and 30% of the contained value may be lost during mineral separation in the case of complex polymetallic sulphide ores. As in the case of mining, the mass flows during concentration will be largely dependent on the grade of the run-of-mine ore. In the case of low-grade metallic ores, particularly non-ferrous ores, tailings typically account for 90% of the run-of-mine ore, although Wills (1997) reports figures of up to 98% - corresponding to a concentration factor of 50. In contrast, the tailings from higher grade non-metallic ores generally account for only 50% of the ore (Wills, 1997). In general tailings from the concentration process will consist mainly of gangue (including host rock and non-valuable ore minerals), as well as minor quantities of valuable or targeted minerals. As in the case of the waste rock, the chemical compositions of the tailings will be dependent largely on the characteristics of the parent ore, with the distribution of ore constituents for any particular concentration process route and technology being dictated mainly by their chemical form and liberation characteristics.

4.2.3 Dewatering

The outputs from solid-solid separation are generally in the form of relatively dilute slurries, typically containing between 50 and 80 % by mass of water, and require dewatering (or solid-liquid separation) in order to recover and recycle valuable water resources. Dewatering techniques can be classified into three main technology groups, viz. gravity separation or sedimentation, filtration and thermal drying.

The most common of the gravity separation or sedimentation techniques, which make use of the differences in the relative densities of solid and liquids, is the cylindrical continuous thickener. Gravity separation is particularly suitable for the dewatering of dilute slurries (> 55% moisture) containing relatively fine solids (0.01-1mm), such as those produced during concentration, and typically reduces the water content to between 55 and 65%.

The most commonly used filtration technique is the continuous rotary vacuum filter. Filtration techniques are normally applied to reduce the water content in slurries from 30-60% to between 10% and 20%, and are thus more suitable for dewatering slurries arising from hydrometallurgical extraction operations (see Section 4.3) rather than the concentration processing stages.

Thermal drying is normally only used to reduce the moisture content of sludges from between 10 and 25% moisture, to approximately 5% or less, and is generally only applied if relatively dry solids are required for packaging or handling purposes.

4.3 Metallurgical extraction

In the case of non-metal resources, the outputs from the concentration processing stage are frequently final products. Concentrates produced from relatively low-grade metal resources are, however, normally intermediate products, requiring further treatment by chemical means in order to produce a sufficiently pure, and hence saleable, product. Conversely, with the exception of heap or dump leaching, most conventional extractive metallurgy process techniques require prior concentration of the low-grade ores.

Chemical extraction, frequently referred to as extractive metallurgy, can be subdivided into two main disciplines, namely hydrometallurgy (entailing the treatment of ores or concentrates with aqueous solutions) and pyrometallurgy (entailing the treatment of concentrates by thermal means). A third discipline, electrometallurgy, is relatively limited in the mining and metal processing sector and hence is not considered here.

4.3.1 Hydrometallurgical extraction

A typical processing flowsheet, as presented in Figure 4.6, indicates that hydrometallurgical processes are comprised of a number of unit operations, the main ones being leaching and dewatering; followed by purification of the pregnant leach solution; and finally recovery of the metal product from the purified solution.

Leaching and liquid-solid separation

Leaching forms the first unit operation in hydrometallurgical processing and is usually performed with a view to selective transformation of valuable or targeted commodity components into a dissolved state for downstream recovery or removal of deleterious impurities. Leaching operations can be divided into two main techniques including dump or heap leaching (applied to crushed low-grade run-of-mine ores) and agitated vat leaching (normally applied to milled high-grade ores or concentrates). Vat leaching techniques can be further divided into ambient pressure leaching (including chemical and bacterial), and high pressure leaching in autoclaves. In many cases the ores or concentrates may be pre-treated using high temperature techniques (such as roasting or calcination) to modify the solubility of the valuable and/or non-valuable components, thereby improving the selectivity of the leaching process.

Regardless of the leach technique, the main reaction mechanisms and related parameters controlling distribution of elements during leaching operations include:

- hydrolysis, which is largely influenced by pH; *and/or*
- complexation, which is mainly influenced by the nature of the complexing ions or leach reagents; *and/or*
- oxidation, which is influenced by Eh (redox potential); *and/or*

- precipitation, which is controlled by pH and, to some extent complexing ions /lixiviants.

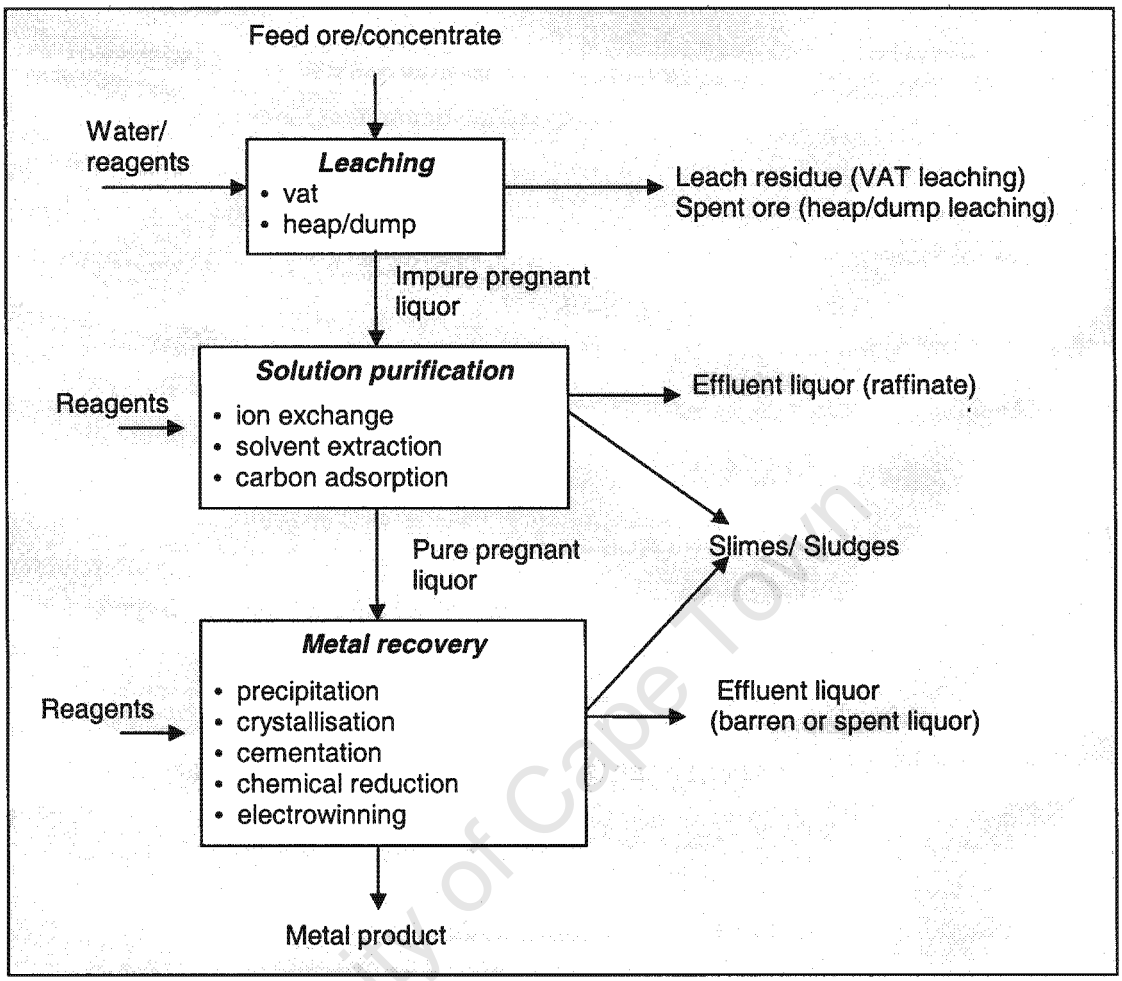


Figure 4.6: Hypothetical flowsheet of the hydrometallurgical processing stage

Leaching can be carried out using a wide variety of leach reagents (water, acids, alkalis and aqueous salts) and under a wide range of pH (1-14) and Eh (reducing-oxidising) conditions, the selection of which will be dependent on the characteristics, particularly mineralogical composition, of the feed material. For the most part, hydrometallurgical leaching reactions are carried out at near ambient temperature (< 25-250°C) and pressure (< 4 MPa) conditions, with the effect of higher temperature and pressure being mainly to enhance leach kinetics. In terms of Eh-pH conditions, leaching is mostly carried out under weakly acidic (pH of 2-4) and weakly oxidising conditions, with acids, particularly sulphuric acid, being the most common leach reagent.

Leach operation outputs include leach liquor, containing the majority (90-98%) of the metal value(s) together with co-leached impurities, and a solid residue, containing the bulk of the unwanted or sub-economic feed material as well as traces (2-10%) of the metal values. These two output streams are separated using conventional dewatering techniques, mainly filtration (see previous sub-section), prior to further processing[6].

[6]Where further processing includes purification of the leach liquor AND disposal of the residue

The majority of the feed material (crushed ROM ore or milled concentrate) thus exits the hydrometallurgical circuit in the form of finely divided wet leach residue, in the case of vat leaching, or crushed spent ore in the case of heap or dump leaching. These residues/ spent ores have traditionally been considered to pose a relatively low risk to the environment and have been land disposed, in many cases without any form of pre-treatment. The potential for prolonged environmental pollution and degradation as a result of discharge of contaminated leachate from leach residue deposits, particularly those from the finely divided and hence highly reactive vat leach residues is, however, becoming increasingly recognised. In many cases, operators are being forced to consider further treatment for safe disposal, or further processing for by-product recovery. Although the latter option has traditionally been considered uneconomical, the economic benefits of product-from-waste recovery, in particular, are likely to grow in importance as costs associated with disposal and associated legal liability increase. Furthermore, as ore deposits become increasingly low-grade and complex, it is becoming increasingly important for the industries to enhance their multi-product capabilities in order to maximize added value.

Solution purification and metal recovery

Leaching and liquid/solid separation is followed by solution purification to further separate leached impurities from the valuable elements, prior to their recovery from the pregnant leach liquor. Various technologies are used for both solution purification and metal recovery, the most common of which are listed in Figure 4.6.

Solution purification and metal recovery operations give rise to slimes and sludges, which accumulate in solvent extraction/electrowinning tanks, as well as effluent liquors containing the co-leached impurities. Slimes and sludges are normally semi-gelatinous materials containing relatively high levels of valuable metals and are thus treated further for metal recovery, rather than being disposed of. Similarly, the stringent standards regarding effluent disposal and water usage dictate that these liquors be treated to remove the bulk of the impurities and produce liquor which is of a suitable quality for recycling purposes. Effluent treatment processes, of which neutralisation is the most common, frequently result in the formation of secondary or "indirect" solid wastes. Although considerably smaller in volume than leach residues, effluent or wastewater treatment residues are mostly finely sized, difficult to filter and handle, and generally have higher metal values than leach residues. As such, these residues can pose an even greater long-term post-disposal risk and are frequently classified as hazardous, requiring disposal in specially designed "hazardous" waste sites. The hazardous nature, coupled with the relatively small volumes and high metal content of the effluent purification residues, will, in many cases, render treatment of these residues economically viable.

4.3.2 Pyrometallurgical extraction

Pyrometallurgical processing is generally limited to concentrate feeds, and normally consists of two main unit operations, viz. thermal processing and refining (see Figure 4.7).

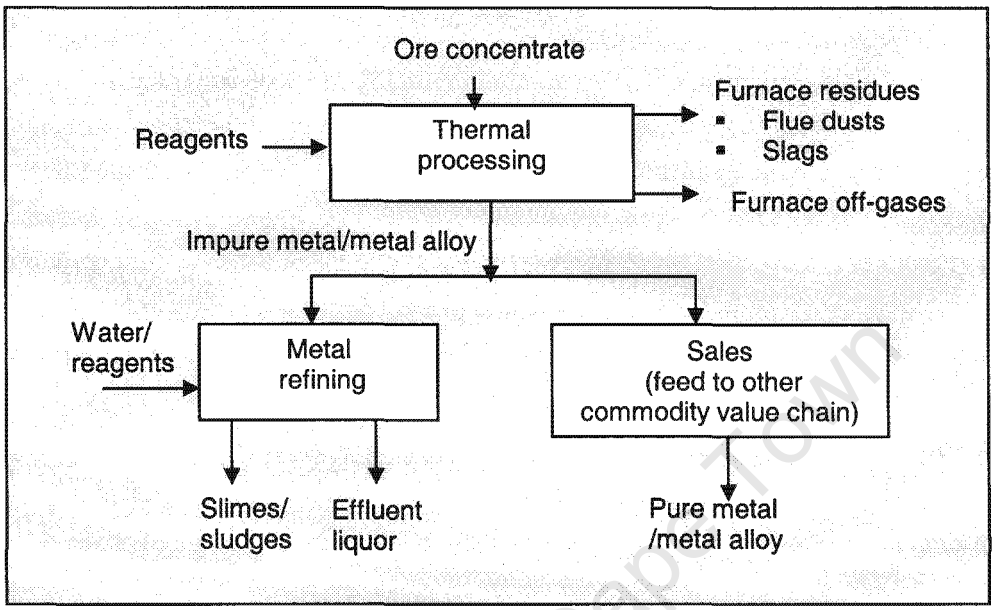


Figure 4.7: General flowsheet of the pyrometallurgical processing stage

Thermal processing

Thermal treatment processes can be sub-divided into smelting and non-smelting thermal treatment processes.

"Low" temperature (600°C-1100°C) non-smelting thermal processes, such as gas phase separations (fuming) or chemical reactions in the solid phase (roasting, sintering, calcining), are normally used as pre-treatment techniques to render feed materials more amenable to subsequent processing operations such as leaching, smelting or, in some cases, even physical processing.

Smelting processes are commonly used for the separation of metal values from non-valuable components in metal-bearing ore concentrates, and utilise considerably higher temperatures than non-smelting processes (>1100°C, and up to 5000°C in the case of plasma-arc smelting). Smelting essentially entails the separation of immiscible, molten liquid phases, in which the metal values occur in the form of molten mattes, metals, metal alloys or metal salts, and the unwanted components in the form of a molten slag and/or off-gas.

Apart from volatile gases, the smelter off-gases generally contain significant quantities of fine grained solid material, blown through and out of the furnace before it can settle in the matte and slag phases, as

well as ore components which are volatile under the smelting conditions. Key reactions and related parameters governing the distribution behaviour of elements during high temperature smelting, include:

- oxidation/reduction reactions, which are largely dependent on the Eh conditions as controlled through the addition of organic reductants or oxidants such as oxygen.
- volatilisation, which is dependent on the partial pressures of the stable forms of the elements at the smelting temperatures
- liquid-liquid separation, which is based on viscosity differences, and is dependent on the stable form (oxide, metals or sulphides) of the elements under high temperature smelting conditions, and the nature of the fluxes added. The viscosities of molten sulphides (mattes) and molten salts are of the same order of magnitudes as those of liquid metals. Oxide melts display a much more complex behavior, their viscosities being highly dependent on metal compositions and temperature, with the viscosity increasing as the SiO_2 content increases.

The most common smelting operation in the metallurgical industry entails the reduction of metal oxides to metals, metal carbides and/or metal alloys using carbon (in the form of coke or char) or carbon monoxide as reducing agents. Reductive smelting using carbon sources is, however, not suitable for the treatment of sulphide compounds, as sulphur anions do not form stable compounds with carbon. Ores or ore concentrates containing valuable elements in the form of sulphides are thus either calcined or roasted prior to smelting, or smelted directly in matte smelting operations. Matte smelting is carried out in the presence of oxygen (or air) and a silica flux, to produce a sulphide matte phase containing the majority of the valuable or targeted elements, and a molten slag, containing the majority of the gangue.

As in the case of physical and hydrometallurgical separations, separation of the valuable and non-valuable elements is never complete, the efficiency of smelting processes typically varying between 95% and 98%. The majority of the solid wastes from pyrometallurgical processes are slags, consisting predominantly of gangue fused with a flux. Most slags are impure silicate glasses in which silica is combined with basic (CaO, MgO) and amphoteric oxides (Al_2O_3, Fe_2O_3) to form silicates, mixture of which have relatively low melting points. Limestone is used as a flux for acid gangue and silica as a flux for basic gangue.

Apart from slags, pyrometallurgical processes also produce gases and particulate solids, recovered from the gas phase by means of gas-solid separators (such as cyclones, bag filters, scrubbers, venturi scrubbers and electrostatic precipitators). Recycling of primary smelter wastes, such as bag filter dusts and scrubber sludges, via complex in-plant and interplant transfer is common within the pyrometallurgical industry.

Metal refining

Liquid-liquid smelters are not very selective in impurity removal, and in most cases the outputs from smelting, including metal-bearing smelter products, slag and dusts, will need further processing to produce marketable products. Metal outputs from smelting operations are frequently purified

electrochemically, with the insoluble impurities reporting to the slimes and the soluble impurities to the electrolyte solution. As in the case of hydrometallurgical processing, the slimes generally contain high levels of valuable metals and are treated further for metal recovery. Soluble impurities are commonly removed from the electrolyte by continuously bleeding part of the electrolyte solution through a purification circuit, which produces a solid phase containing the unwanted impurities.

4.4 Summary and concluding remarks

Both the selection of ore extraction and beneficiation processes, and the characteristics of the waste outputs generated, are highly dependent on the characteristics of the ore deposit, particularly in terms of element concentration and mode of occurrence (form and distribution). For any specific ore body, however, the distribution of ore components, and hence the compositions of each waste output stream, will be directly influenced by the individual unit process operations, each of which is dictated by a set of conditions relating to technological performance on a reactor level.

In line with this, the specific aim of this chapter of the thesis was to review the relationship between the various unit processing operations and the generic characteristics of the waste outputs typical of the primary mineral based resource industries, and to identify the key factors, in terms of technology variables and parameters, influencing such. The information derived from this review and assessment is summarised in Table 4.2.

As demonstrated within Chapter 5 of the thesis, this qualitative information plays an important role in addressing data gaps and inconsistencies pertaining to available process inventory data and, ultimately, in predicting key environmental characteristics of solid waste outputs. More specifically, this information serves to assist in the definition of the system boundaries and relevant unit processes; collection of appropriate process data and background information; and the meaningful selection and application of scientific techniques and methods for predicting element deportment during ore beneficiation.

Application of the fundamental understanding and criteria developed within this particular chapter for predicting element distribution behaviour during ore beneficiation is demonstrated for the case of copper sulphide ore concentration in Chapter 6 of the thesis. Chapter 8 demonstrates application for the subsequent pyrometallurgical extraction of copper sulphide concentrates, as a function of smelter technology choices.

Table 4.2: 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 dependent 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 dependent 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

"The cornerstone in environmental assessment procedures is modelling of differences in inputs and outputs" Wenzel, 1999

5

A Generalised Methodology for Predicting Element Distribution

Thus far, this thesis has developed a qualitative understanding of the key factors influencing element speciation and distribution behaviour across the ore formation → ore extraction & beneficiation → solid waste disposal → leachate generation mechanistic chain. On this basis, generic protocols for addressing current data gaps and deficiencies pertaining to the chemical compositions of ore deposits and beneficiation input-output streams (Figure 4.3 in Chapter 4), and subsequently for screening final waste constituents in terms of relative environmental significance (Figures 2.9 and 2.10 in Chapter 2), have been proposed. This particular chapter is concerned with the methodological components of these procedural frameworks, which can be summarised in three main tasks, viz:

Task 1: Collation and review of available and relevant empirical data and information for the system under consideration

Task 2: Theoretical assessment of the distribution behaviour, associations and chemical properties of elements during ore formation, beneficiation and solid waste disposal, on the basis of fundamental chemical and thermodynamic principles

Task 3: Reconciliation of available empirical and theoretical data to generate a comprehensive and quantitative list of input-output stream compositions and/or potential element distribution factors, which can be combined with mass flows to develop mass balance spreadsheets and, ultimately, screen and rank constituents in terms of environmental significance.

As demonstrated in Figure 5.1, these tasks can be broken down further into a number of technical elements which are essentially the scientific techniques of obtaining, processing and presenting the required data and information. Each of these techniques can, furthermore, cover a wide range of scientific disciplines and even greater number of scientific methods, each with their own strengths, limitations and purposes. Whilst this chapter will include a brief overview of selected techniques and associated methods, a comprehensive review and assessment of all these techniques is beyond the scope of this thesis. The intention is rather to develop general guidelines in terms of the selection and application of appropriate scientific techniques and methods, and to provide some illustrative

examples by way of demonstration. As such this chapter provides the basis for the case studies in Chapters 6 to 8, in which the methodological tasks and associated technical elements are applied to derive data pertaining to element distribution behaviours, input-output stream compositions and environmentally significant waste characteristics for selected processes and operations associated with primary copper metal production.

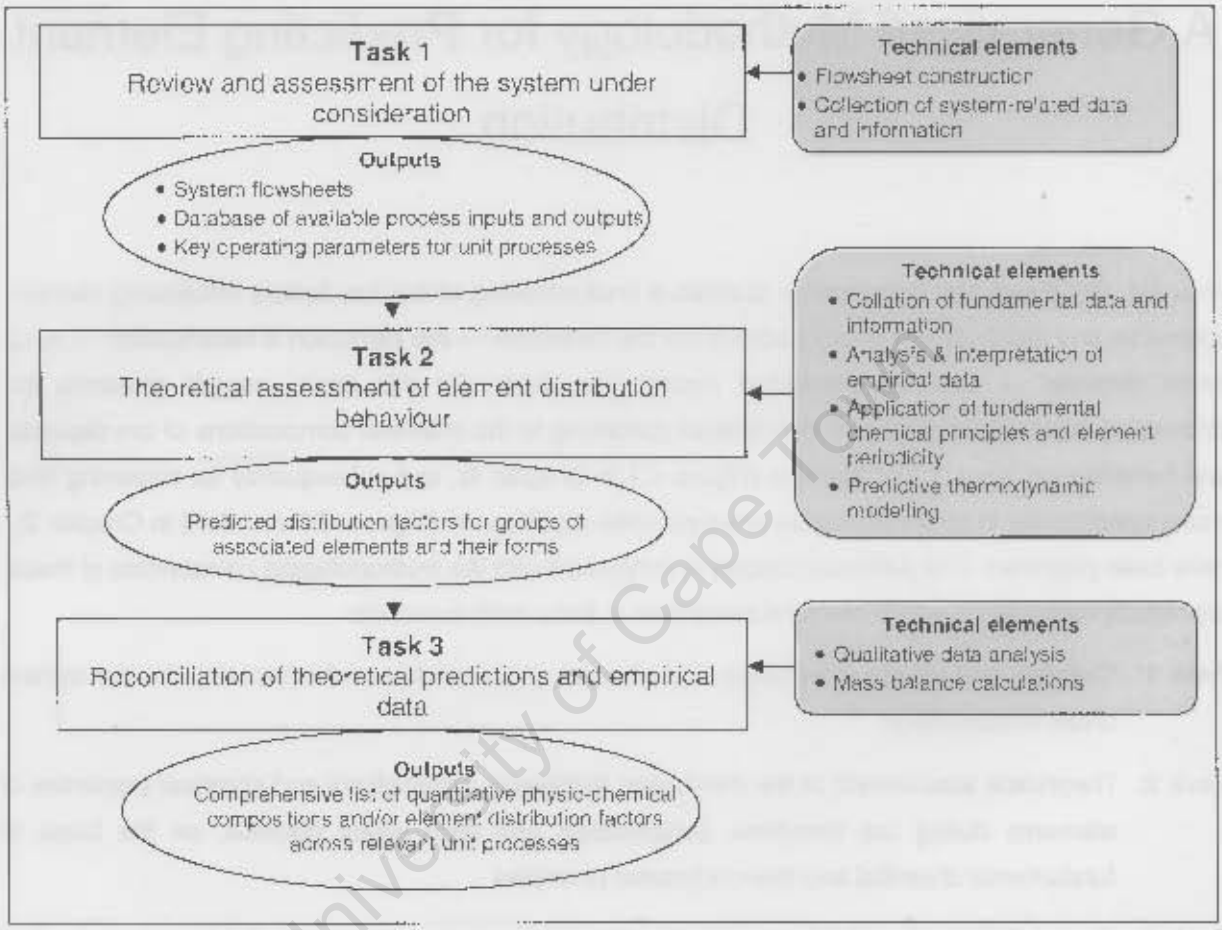


Figure 5.1: Generalised methodological framework for predicting data and information pertaining to element distributions, process inventories and solid waste characteristics

5.1 Task 1: Review and assessment of the system under consideration

An analysis of the system under consideration is the first step in the proposed methodology, and perhaps also the most important. In particular, such an analysis serves 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

This task essentially entails two technical components. In the first instance the system is "mapped" by means of a flowsheet which identifies all relevant processes and arranges them in relation to one another. This flowsheet serves as a practical aid to the second technical element i.e. collection of all available and relevant data and information pertaining to the identified processes.

5.1.1 Flowsheet construction

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 study. On the basis of the understanding gained from the reviews in Chapters 2 to 4, the system boundary of relevance to this study (i.e. for predicting the key environmental characteristics of solid mineral wastes on the basis of their origins and source) will encompass ore formation; ore extraction and beneficiation; disposal of final solid wastes; and leachate generation as the main processing stages. The solid waste deposit is thus central to the system boundary, illustrated in Figure 5.2, with links extending upstream to the formation of ore deposits (waste origins) and processing thereof (waste source), and downstream to the formation of environmental emissions. In this way the conventional "cradle-to-gate" system boundary for describing mineral resource-based process operations is extended 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.

Figure 5.2: System boundary for predicting key environmental characteristics of solid mineral wastes

Further division of the main processes defines the inputs and outputs across sub-processes or individual operations, which require characterisation in terms of mass and component flows. Discussions in previous chapters have highlighted the complex and varied nature of each of the main processing stages depicted in Figure 5.2, particularly in terms of the vast number of individual operations and the complex compositions of the associated input-output streams. These complexities are reflected by the hypothetical flowsheet in Figure 5.3, which includes both the relevant 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.

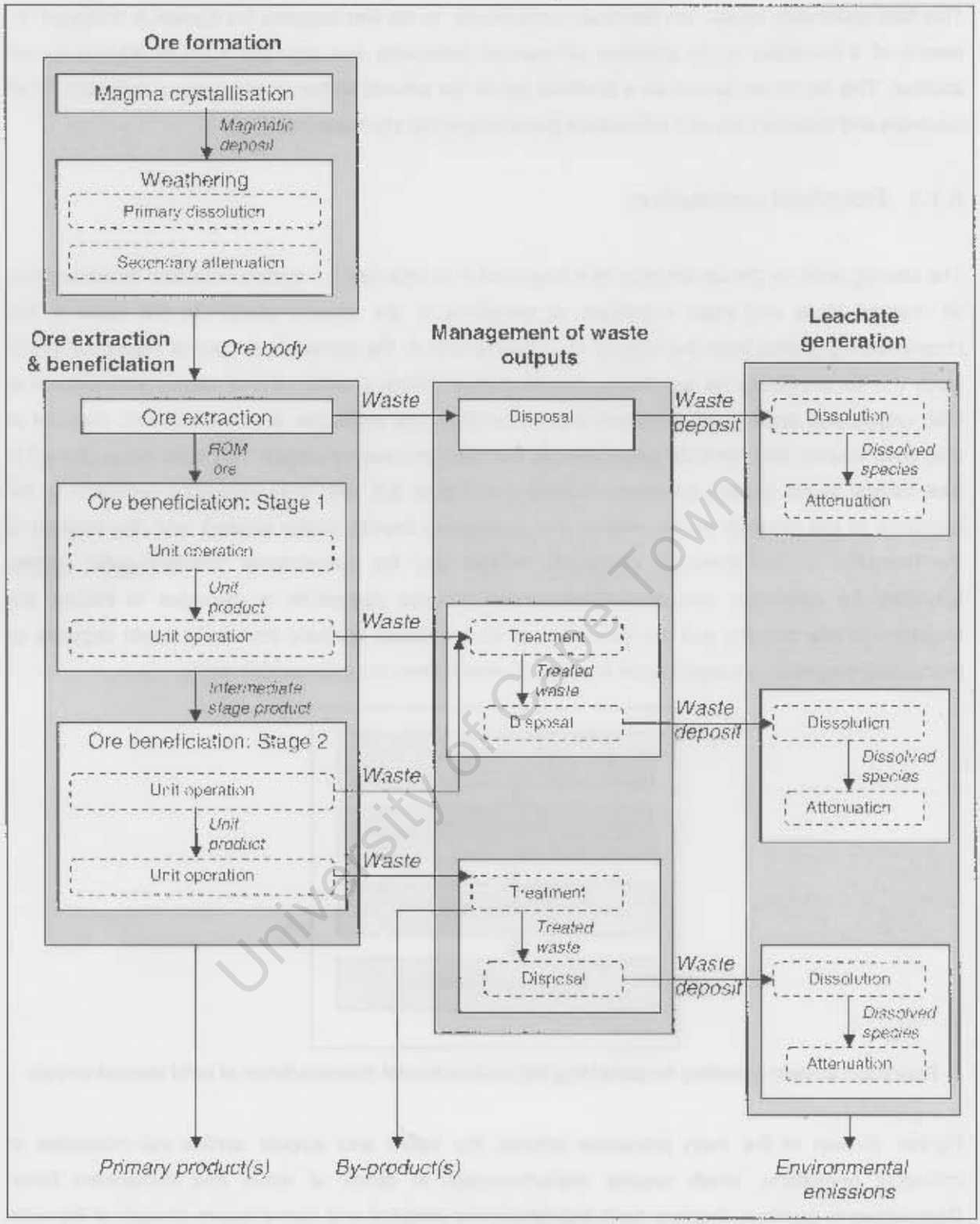


Figure 5.3: Hypothetical flowsheet of unit processes and inventory streams requiring characterisation

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. In terms of this particular study, however, the selection and aggregation of unit processes will be dictated mainly by their relevance in terms of their direct influence on the generation and chemical compositions of waste outputs. In this regard any unit operation not directly responsible for the generation and/or chemical composition of a waste output can generally be combined with upstream or downstream operations in a single unit. As an example, whilst wastes frequently exit a processing stage at the liquid/solid separation unit, it is the upstream processes (such as leaching or flotation) which are largely responsible for their generation and chemical composition. In such cases the liquid/solid separation operations (e.g. thickening and filtration) can be combined with the relevant upstream operation in a single unit. This unit is often defined by the generating process (e.g. as "leaching" or "flotation"). Milling prior to solid-solid separation is another example of an operation which does not play a key role in the generation or chemical compositions of waste outputs streams, and can thus be combined with the relevant downstream solid-solid separation unit[7].

The application of these criteria is supported by the hypothetical flowsheet in Figure 5.3.

5.1.2 Data collection

The second technical component of this task entails the collection of available and relevant data and information to describe the relevant unit processes and inventory streams identified during construction of the system flowsheet. In line with the study objectives, two types of required information can be defined, viz:

1. Stream flow information, including physio-chemical compositions and mass flows of the input-output streams
2. Process performance information required to address data gaps pertaining to stream flow information, including:
    - extent of input stream conversions and/or distributions during processing, also referred to as "reactor efficiencies" or "conversion factors" (see discussions by Reuter, 1998 ; Stewart and Petrie, 2006).
    - measures of the key operating parameters governing such (temperature, pH, reagents, redox potential (Eh), oxygen partial pressure, etc)

[7] In the case of a more holistic performance evaluation, milling and flotation would need to be identified separately on the basis of their relative energy intensities

These information requirements and their inter-relationships are represented by the generic unit operation in Figure 5.4.

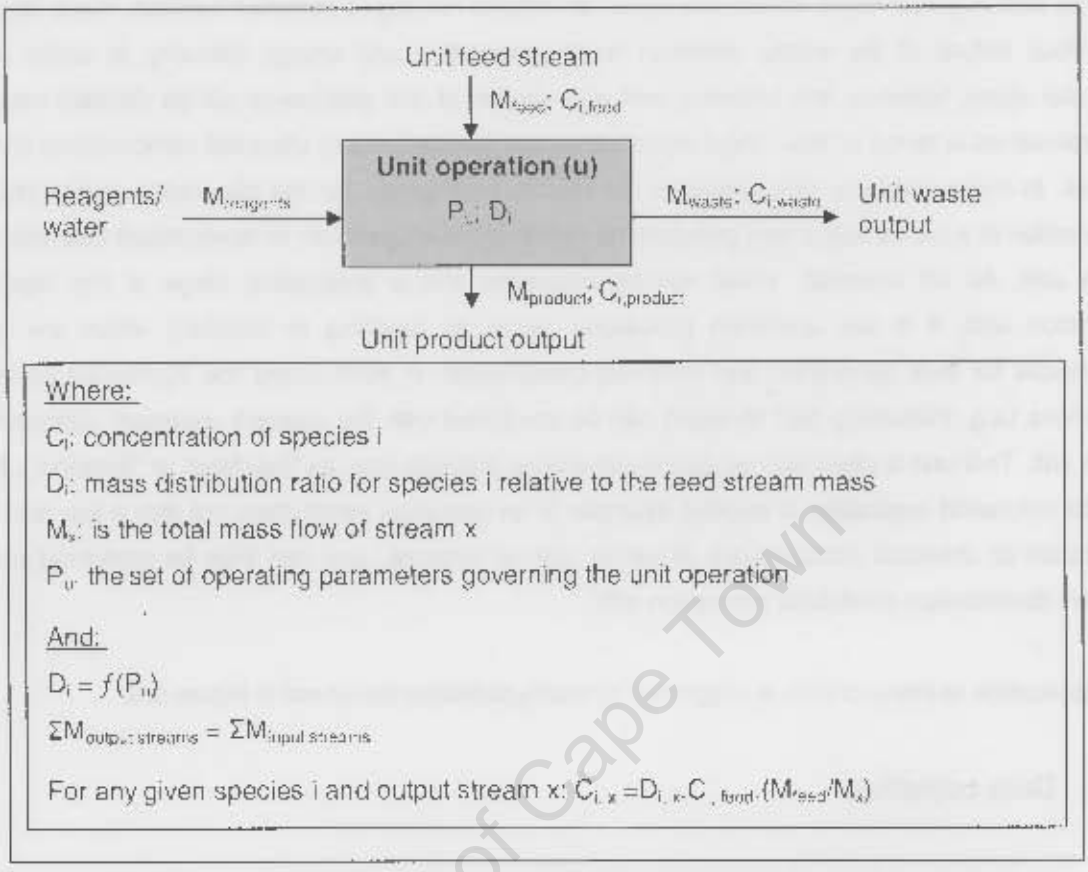


Figure 5.4: Generic unit process within a flowsheet (modified from Stewart et al, 2003a)

Stewart & Petrie (2006) have applied these information types in the development of LCIs (Life Cycle Inventories) for primary processes across entire mineral sectors. In its current form, however, these inventories, 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). Expansion of the flowsheet to facilitate assessment of the potential water and land-related impacts associated with mineral resource-based process operations on a project level has already been discussed in the previous section. In accordance with the review in Chapter 2, expansion is also required in terms of current LCI-type databases so as to include both the total concentrations and speciation (or form) of individual trace metals and salt-forming constituents within the relevant input-output streams. It is also important to ensure that these inventory databases are as detailed and disaggregated as possible. This will aid transparency and increase the accuracy and certainty of the subsequent environmental assessment tasks.

There are several potential information sources for supporting collection of available data in line with the above-mentioned requirements. Stewart & Petrie (2006) provide a comprehensive list of information sources used in developing first order LCIs for the minerals industry sectors, which includes

government waste inventory reports; academic journals; reference books; newspapers and industry press; company annual reports; information pamphlets, environmental impact statements and other statuary documents; as well as interviews and plant visits. Not all of these will, however, be suitable for sourcing detailed process-specific information consistent with the requirements of this study. Applicable data and information pertaining to process stream flows and unit performance will mainly take the form of empirical plant data and/or data from testwork programmes on a laboratory or pilot-plant scale. Although some of these data will be available in the published literature (e.g. academic journals and reference books), much of the 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. As already discussed in Chapter 1, such information is frequently considered proprietary, and is not available outside of the specific organisation.

5.2 Task 2: Fundamental assessment of element distribution behaviours

The second step in the proposed methodology entails the theoretical assessment of the potential element distribution behaviours and associations within the relevant unit processes or operations, including the relative extents of:

- enrichment in ore deposits
- deportment during ore extraction and beneficiation
- availability for release from solid wastes in a disposal scenario

In line with the first-order[8] nature of this study, element distribution behaviours and trends are expressed as qualitative (e.g. high, medium, low) or semi-quantitative (covering a range of potential values) measures of the typical, rather than absolute, extents of element enrichment, deportment and/or environmental availability. These measures can either take the form of mass percentages or mass ratios (commonly termed factors) which, when combined with mass flow information, will enable element concentrations in the unit output streams to be calculated (see Figure 5.4).

Despite the first-order nature of element distribution data, it is important to ensure that these values are not arbitrary, but are derived through the application of scientifically valid and appropriate techniques and methods, which can be divided into four main types or categories, viz:

- Collection of data and information pertaining to the fundamental properties of the elements and their compounds.

[8] In accordance with previous discussions in Chapter 1, data uncertainties of between 25% and 40% in the project conceptual and early design stages is both acceptable and, in terms of data and information management, necessary (Douglas, 1988).

- Analysis and interpretation of relevant empirical data from fundamental research programmes.
- Application of the fundamental chemical principles of element periodicity.
- Predictive thermodynamic modelling.

The selection and application of the most appropriate techniques for the derivation of element distribution factors on the basis of the above-mentioned criteria is not a simple or trivial matter, and requires a clear understanding of the criteria or factors influencing element distribution, as derived within Chapters 2 to 4 of the thesis and summarised in Table 5.1.

Table 5.1: The overarching criteria influencing element distribution behaviour across the ore formation → ore extraction & beneficiation → solid waste disposal → leachate generation system boundary (based on discussions in Chapters 2-4)

Unit process description	Controlling criteria
Aqueous systems including: • Weathering of primary ore deposits and formation of sedimentary deposits • Hydrometallurgical extraction and metal refining operations during ore beneficiation • Weathering of final wastes in a disposal scenario	Relative solubilities or mobilities of the stable forms of the elements, as governed by primary dissolution and secondary attenuation reaction mechanisms and influenced largely by the pH, Eh and concentrations of the major complexing ions in the leach solution or pore waters.
Thermal systems including: • Primary deposition of magmatic ore deposits • Pyrometallurgical extraction operations during ore beneficiation	Relative ionic radii and thermal properties of the stable forms. The latter pertains largely to viscosities and volatilities, as a function of furnace operating parameters such as temperature, redox conditions (reducing or oxidising), and the nature of the reagent inputs (fluxes, reductants and/or oxidants)
Solid-solid separation systems including: • Ore extraction or mining • Physical concentration operations during ore beneficiation	The stable forms of the elements and their relevant fundamental properties, e.g. magnetic susceptibility, density, particle size etc.

In some instances, data pertaining to these criteria and, subsequently the element distribution factors, may be derived directly from fundamental data (e.g. temperature related viscosities of compounds during reductive smelting) reported in the open literature (e.g. reference books and academic journals). In many instances, however, the relevant databases are either incomplete or non-existent. This is particularly the case for the minor and trace elements and their compounds, the chemical properties and behaviours of which remain largely unquantified and, in some instances, unqualified. Even where available, fundamental data (e.g. solubility products, formation constants) are often only valid for a specific set of "standard" conditions and cannot be directly extrapolated to the mineral resource-based aqueous and thermal processing operations described in Table 5.1. In such cases, a meaningful

estimation of the element distributions within a given system will rely on the application of a combination of two or more of the above-mentioned predictive techniques.

As already alluded to in this chapter, these techniques cover a wide range of available databases and scientific methodologies. Each of these has its limitations and strengths, and can vary quite considerably in terms of complexity, procedural detail, costs and, in some cases, even its core purpose. The use of detailed and complex models and empirical testwork programmes for the derivation of first-order element distribution factors is, however, unlikely to be necessary or warranted. Such methods are time-consuming and costly, and normally require detailed and accurate input data and information in order to deliver reliable results. In the case of the mineral resource-based processing systems, particularly the leachate generation units, such input is generally either unavailable or highly uncertain, particularly in the early developmental stages of a project. It is postulated that the application of a number of relatively simple predictive methods in a manner which allows for validation of the consistency of results will provide sufficiently reliable estimates of element distribution factors (i.e. measures consistent with early project stage requirements in terms of accuracy), whilst ensuring that resource requirements (including information, time and costs) remain manageable.

Section 5.2.1 provides a brief overview of the more relevant predictive techniques and methods, supported by a few examples to illustrate the practical application thereof. These methods and examples support the copper case studies presented within Chapters 6 to 8 of this thesis.

5.2.1 Overview of selected data and methods for the prediction of element distribution factors

Collection of data pertaining to fundamental properties of the elements and compounds

Data pertaining to the fundamental physical and chemical properties of the elements, naturally-occurring minerals and inorganic compounds of the metals and semi-metals can mainly be sourced from reference and handbooks. Other potentially useful sources of information include academic journals; the databases of predictive thermodynamic models; and organisations involved in fundamental R&D studies for the minerals industries. Some examples of fundamental data and information sources of relevance to this study are provided in Table 5.2.

Table 5.2: Properties of inorganic elements and minerals: useful data sources

Information type	Examples of sources
Thermodynamic constants: e.g. K_f, K_{sp}, ΔG_f°, ΔH_f°	Reference books: Brookins (1988); Chase et al (1985); Cotton & Wilkinson (1962); Elliot & Gleiser (1960-63); Garrels (1960); Knacke et al (1991); Kneen et al (1972); Lide (1997); Moore (1990); Price (1998); Robie et al (1978) Rosenqvist (1983), Woods & Garrels, 1987; Zeimack, 1992 Thermodynamic model databases: MINTEQA2 (Allison et al, 1990 and US EPA CREAM, 2005), OLI (OLI Systems Inc, 1991); PHREEQE (Parkhurst, 1995); HSC Chemistry® for Windows, version 5.1 (Outokumpu, 2002)
Physical properties: e.g. melting and boiling point, vapour pressure, density, magnetic susceptibility, thermal conductivity	References above; Hayes (1985); Kelly & Spottiswood (1982)
Periodic element properties e.g. ionic and atomic radii, electronegativities, ionization energies, electron affinities	Cotton & Wilkinson (1962); Kneen et al (1972)
Average crustal abundance	Cotton and Wilkinson (1962); Cox (1995); Thornton (1983)

Analysis of data from relevant empirical programmes

Data from fundamental laboratory-scale R&D programmes can provide valuable information in terms of the potential distribution of elements across the ore formation → ore extraction & beneficiation → waste disposal → leachate generation mechanistic chain. In particular, the potential availability or mobility of elements during chemical weathering and leaching of minerals in aqueous systems can be inferred from the results of empirical sequential chemical extraction (SCE) as well as batch and/or column leach tests.

- Sequential chemical extraction (SCE) tests:

These tests entail subjecting either different samples of the material to leachants of various strengths in a series of parallel tests, or subjecting one sample to differing strengths or types of leachants sequentially. Although 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, a number of authors (see for example Carlsson et al, 2002; Dang et al, 2001; Dold, 2003; Dold & Fontbote, 2001; Guirco et al, 2000; Hansen, 2004; Leinz et al, 2000; Mitchell et al, 1994; van Herck & Vandacasteele, 2001) have developed and applied modified versions of the traditional SCE tests to inorganic solid

wastes. These "modified" SCE tests are designed to provide quantitative data pertaining to the forms in which major components occur, and the manner in which the trace to minor components are associated with these major minerals. On the basis of these results predictions can be made pertaining to the potential modes of occurrence and mechanisms that are likely to control the availability of elements under disposal conditions, with each fraction representing a different mode of occurrence and potential controlling chemical reaction mechanism (see Table 5.3)

Table 5.3: Potential modes of occurrence and leach behaviour of the elements 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 dependent 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 dependent 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 dependent 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 dependent 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

This information can, in turn, 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 constituents that are associated with the residual fractions are unlikely to occur to a significant extent within the time-scale of concern (in accordance with discussions by Hansen (2004), such time-scales are typically considered to be in the order of 100 years, although a longer time period of 500 years may be more appropriate for metals impacts). 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, have been developed by Galan et al (2003) and Hansen (2004). Despite the wealth of information that can be derived from SCE tests, there is currently uncertainty regarding the accuracy of the quantitative results, and unless verified by other characterisation tests, the results of the SCE tests should be considered as only semi-quantitative estimates of metal partitioning.

- Standard laboratory-scale leach tests

Whilst the SCE tests described above generate data and information pertaining to the inherent waste properties influencing the potential environmental availability, leach tests are specifically designed to generate data which can be directly interpreted in terms of potential availability of contaminants for release to the environment under actual or typical disposal conditions. As already discussed in chapter 1 of the thesis (see Tables 1.1 and 1.2), a number of empirical waste tests have been developed for characterising the leach behaviour of solid wastes, each of which has its limitations, and is specifically designed to reveal only one or two aspects of the leaching behaviour of the solid under investigation. A fundamental study of the leach behaviour of mineral wastes in solid deposits, combined with a comprehensive survey and assessment of standard empirical methods for the characterisation of such, has indicated that, in general, laboratory-scale leach tests can be considered to provide a reasonable, if somewhat exaggerated, estimate of the potential availability of contaminants for release under field conditions, providing that:

- all chemical reactions are sufficiently accelerated such that equilibrium or near equilibrium is achieved between the waste and the leachant during the test period.
- the test conditions, particularly with respect to liquor compositions (in terms of major ions, pH and Eh) and L/S ratios, are similar to that expected in the deposit.

Unfortunately, conditions within the solid mineral waste deposit are frequently unknown, whilst many of the key reaction mechanisms controlling the leach behaviour of primary mineral phases are extremely slow, and consequently cannot be simulated in short-term leach tests. On their own, standard laboratory leach tests are thus generally deficient in terms of their ability to provide a realistic estimate of the potential availability of contaminant from solid mineral wastes over the long- term.

Predictive thermodynamic modelling

Theoretical predictions of element distribution behaviours in mineral resource-based process systems can 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). The HSC Chemistry® for Windows model, as well as FactSage™ 5.4 (CRCT-ThermFact Inc and GTT-Technologies, 2005), can also be used to model thermal (i.e. high temperature non-aqueous) systems. 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 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.

One of the main disadvantages of predictive thermodynamic models in terms of generating first-order element distribution data is that they require fairly extensive input data. Data requirements include element activity coefficients and other aqueous properties (Eh, pH), as well as the nature and concentrations of adsorbing solids. Predictive thermodynamic models also presuppose knowledge of all prevailing reaction mechanisms and stable chemical phases, and associated equilibrium constants. Unfortunately, most complex systems, particularly solid mineral waste deposits, remain poorly understood, and the required model input information and data is frequently either unavailable or highly uncertain. This problem is aggravated by the fact that many of the models do not permit the user access to the model database, which reduces the transparency and adds to the uncertainty of the model predictions.

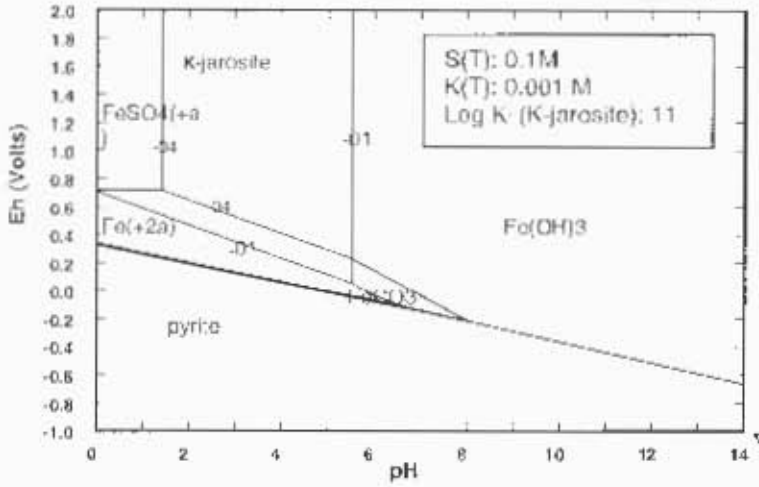
Published thermodynamic databases and diagrams, established by various authors on the basis of fundamental thermodynamic principles, provide a potentially useful source of data and information for predictive models. Examples include Eh-pH diagrams, which identify regions of dominance for the

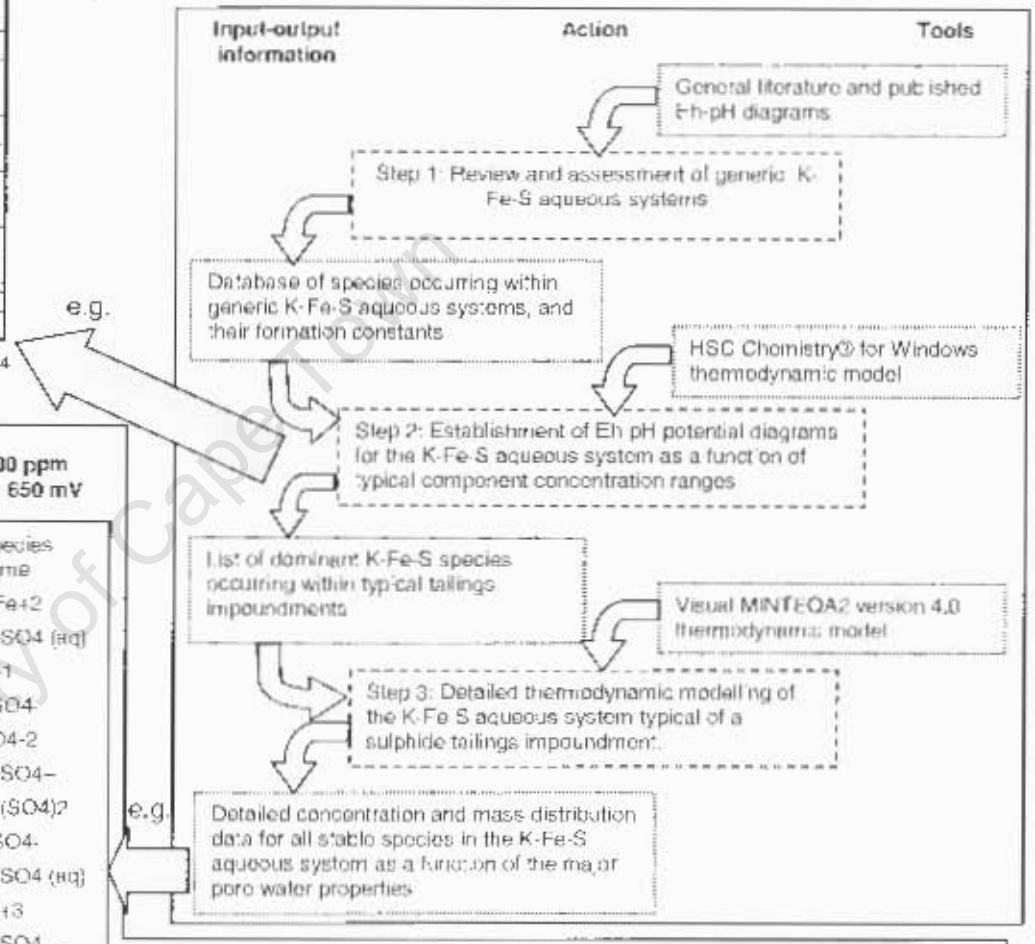
chemical forms in which individual elements may occur in aqueous systems as a function of redox potential and pH, and Ellingham diagrams as reported by Rosenqvist (1983), which depict the stability of various metal compounds as a function of temperature in thermal systems. Such information and data are, however, frequently derived for specific, narrowly-defined and relatively simple systems (i.e. containing relatively few components at specific concentrations), and cannot be readily extrapolated to the conditions typical of mineral-based resource processing systems.

The combined application of published thermodynamic data and predictive thermodynamic models having different attributes and levels of complexity for the semi-quantitative prediction of iron attenuation (through secondary precipitate formation) and speciation within a sulphide tailings impoundment, is illustrated in Box 5.1. This exercise forms part of the Chapter 7 case study, in which the constituents within a tailings waste from the milling and flotation of a porphyry-type copper sulphide ore are screened and ranked on the basis of their hazard potential and environmental availability in a disposal scenario (see Section 7.2).

In this particular exercise, published thermodynamic data and Eh-pH diagrams (Baron & Palmer, 1966; Bigham et al, 1996; Blowes et al, 1998; Brookins, 1988; Carlsson et al, 2003; McGregor & Blowes, 2002; Moncur et al, 2005; Pourbaix, 1996) provide a preliminary database of possible species, and their formation constants, in the system of relevance in terms of the availability of iron in sulphide tailings impoundments i.e. the K-Fe-S-H_2O system. This information is then coded into the Eh-pH diagram module of the HSC Chemistry® for Windows thermodynamic model (Outokumpu, 2002), selected specifically for its user-friendly diagram graphics and easily adjusted database. This allowed for the addition of Schwertmannite ($Fe_8O_8(OH)_6(SO_4)_2$), which is not included in either the standard HSC or Visual MINTEQA2 databases, as well as an analysis of the effects of the various formation constants reported for ironhydroxy and ironhydroxysulphate precipitates (see Appendix 7.3 in Chapter 7). The Eh-pH diagrams generated by this model provide an indication of the stable K-S-Fe-H_2O species likely to occur within a sulphide tailings impoundment, as a function of the component concentrations and reported species formation constants. This information is subsequently coded into the Visual MINTEQA2 version 4.0 model (US EPA CREAM, 2005), to generate detailed K-S-Fe-H_2O speciation and distribution data ranges for the sulphide tailings impoundment system, as a function of likely pore water chemistry in terms of Eh, pH and component concentrations. Although fairly resource-intensive (in terms of input data and information), this model is particularly attractive for simulating dilute (ionic strength < 0.5 M) aqueous geochemical systems, as it includes advanced surface complexation calculations; can accommodate a range of input parameters and variables; and provides extensive output data in a spreadsheet format which is easy to interpret.

Box 5.1: Semi-quantitative prediction of the potential extent of attenuation and speciation of iron within a typical sulphide tailings impoundment





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	0.0033	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-20
KSO4-	2.22E-10	1.86E-10
OH-	3.85E-12	3.17E-12

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
	0.24	Fe(OH)2+

Solids	Concentration (M)
K-Jarosite	2.58E-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

Fundamental periodic properties of the elements (element periodicity)

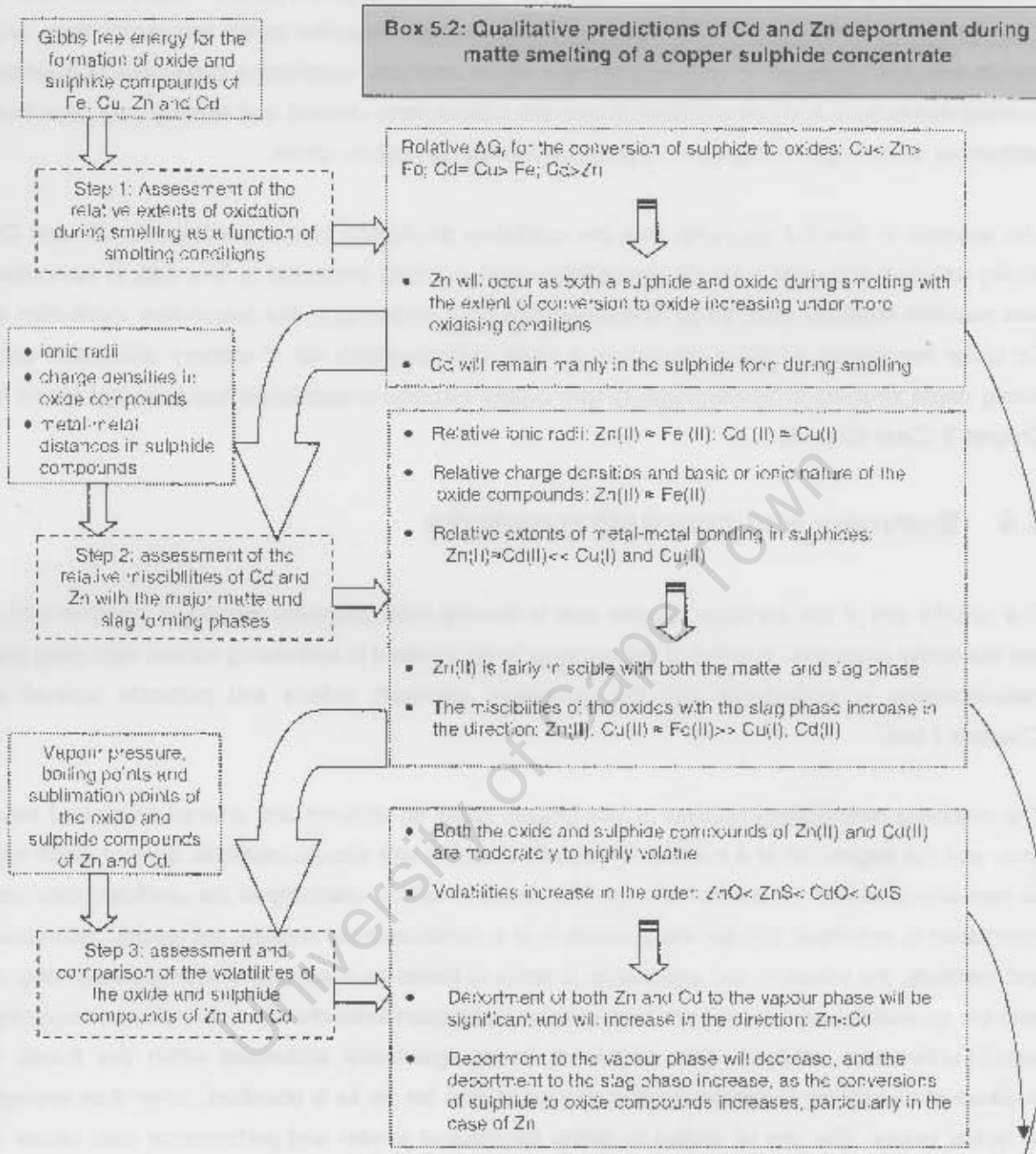
Another important, but largely under-utilised predictive methodology entails analysis of the periodic chemical properties and trends of the elements, commonly referred to as element periodicity. Predictions on the basis of element periodicity are underpinned by the fact that element distribution is governed by their fundamental properties, which dictate the stable element and associated chemical behaviour under a given set of conditions. Important element properties that can be correlated with a wider range of chemical distribution behavioural patterns include their electronic configurations, atomic masses, ionic radii and charge densities (Kneen et al, 1972). Furthermore, certain elements have similar properties and hence can be expected to be present in similar forms and exhibit similar behavioural patterns under a specific set of conditions. These associated trends and patterns are frequently reflected by diagrams and tables in which elements are arranged and grouped accordingly. Examples include the periodic table (see Figure 3.4 in Chapter 3); the ionic radii vs. charge diagram (see Figure 2.5 in Chapter 2) which groups elements according to their stable element forms in natural aqueous environments; and the charge density vs. ionic radii diagram (see Figure 3.6 in Chapter 3) which groups metal oxides in accordance with their basicity and relative thermal stabilities. The fact that elements can be grouped in accordance with common properties and behaviour patterns allows one to pre-suppose or predict similar deportment behaviours for other elements in the same group.

An example of the application of periodic chemical properties and trends of the elements for the qualitative prediction of the relative deportments of Zn and Cd during matte smelting of a copper sulphide concentrates is illustrated in Box 5.2. This exercise forms part of the case study in Chapter 8 of the thesis (see Section 8.2).

5.3 Task 3: Reconciliation of empirical data and theoretical predictions

In the broader sense data reconciliation is concerned with the adjustment of measured variables and the estimation of unmeasured variables to meet mass balance requirements, and is commonly used to improve precision in metallurgical or metal balances through the application of numerical data reduction techniques (see for example Chakraborty & Deglon, 2006). Such techniques are, however, not suitable for reconciling incomplete lists of empirical data from dispersed sources with qualitative or semi-quantitative predictions. Reconciliation in the context of this particular study thus essentially entails the harmonisation of available empirical data with the fundamental understanding gained in task 2 of the methodology (Section 5.2), and as such does not involve the use of numerical techniques.

Box 5.2: Qualitative predictions of Cd and Zn deportment during matte smelting of a copper sulphide concentrate



	Qualitative predictions for Cd deportment	Qualitative predictions for Zn deportment
Vapour phase	Significant, decreasing slightly as the conditions become oxidising	Moderate, decreasing under strongly oxidising conditions
Matte phase	Partial	Partial
Slag phase	Low, increasing slightly as the conditions become more oxidising	Partial to moderate, increasing as the conditions become more oxidising

In the first instance, the qualitative or semi-quantitative element distribution predictions (task 2 of the methodology) are used to interpret and rationalise the available empirical data, collected within task 1. This step serves to validate the theoretically predicted element behaviour trends and associations, and identify possible anomalies in the empirical data. In the next step, quantitative predictions of potential element distributions and concentration ranges are subsequently derived, and existing data gaps thus addressed, on the basis of the element periodicity principles outlined above.

The example in Box 5.3 illustrates how the qualitative distribution factors predicted for Zn and Cd during smelting of copper sulphide concentrates (see example presented in Box 5.2), is reconciled with available empirical data, so as to address data gaps pertaining to the quantitative distribution of Cd under moderately oxidising conditions. A more comprehensive list of element distribution data during matte smelting of typical porphyry-type copper sulphide concentrates has been generated in Chapter 8 (Case Study 3).

5.4 Summary and concluding remarks

The specific aim of this particular chapter was to develop methodological guidelines, together with a few illustrative examples, in terms of the technical tasks involved in addressing current data gaps and inconsistencies in accordance with the conceptual approach, criteria and protocols outlined in Chapters 1 to 4.

The proposed methodology outlined in this chapter relies on different and diverse sources of input data, and the application of a number of scientific disciples and specific methods, each of which has its own strengths and limitations. Although first-order in nature, credibility of the predicted data and information is enhanced through the application of a combination of suitable, yet simple, techniques and methods, the selection and application of which is based on a comprehensive understanding of both the mineral-based resource process systems and fundamental chemical principles underpinning such. Furthermore, although data uncertainty is not specifically addressed within this thesis, a measure of uncertainty is implied by using ranges of data (as far as is possible), rather than average or typical values. The use of ranges to define input-output stream and performance data values is consistent with the extremely variable nature of natural ore deposits and mineral-based resource processing systems, as well as the iterative nature of process evaluation and design procedures. In according with these procedures data uncertainty will gradually be reduced (and associated ranges of values thus narrowed) on progressing from the conceptual to the final design and implementation stages.

The methodological tasks and associated technical elements outlined in this chapter are applied to derive data pertaining to element distribution behaviours, input-output stream compositions and environmentally significant waste characteristics for selected processes and operations associated with primary copper metal production in Chapter 6 to 8.

Box 5.3: Quantitative predictions of Cd and Zn deportment during matte smelting of a copper sulphide concentrate: Reconciliation

Summary of available empirical and predicted qualitative deportment results (after Biswas & Davenport, 1994; Hoh et al, 1983; Riveros & Utgard, 2003)

	Moderately oxidising conditions		Strongly oxidising conditions	
	Cd	Zn	Cd	Zn
Vapour phase	Extensive **n/a**	Moderate **40**	High **64**	Partial-moderate **23**
Matte phase	Partial **n/a**	Partial **15**	Partial **17**	Partial **11**
Slag phase	Low **n/a**	Partial-moderate **45**	Low-partial **19**	Moderate-high **66**

Where:

- moderately oxidising conditions are assumed to correspond to a 55% Cu matte grade
- strongly oxidising conditions are assumed to correspond to a 75% Cu matte grade
- qualitative deportment data is derived from the exercise presented within in Box 5.2
- quantitative data (in bold) is accessed from the literature (see Table 8.1 in Chapter 8)
- n/a denotes not available

Step 1: Rationalisation and interpretation of the available empirical data on the basis of the outcomes of task 2 (see Box 5.2)

- The deportment of Zn to the slag phase under moderately oxidising conditions is consistent with the relatively high affinity of Zn for oxygen (in comparison to Cu), resulting in fairly extensive conversions of the sulphide to the oxide under most smelting conditions
- The increase and decrease in the deportment of Zn to the slag and vapour phases respectively as the conditions within the smelter become more oxidising can be attributed to a corresponding increase in the conversion of ZnS to ZnO.
- The higher deportment of Cd to the vapor phase and lower deportment to the slag phase relative to Zn under highly oxidising condition is consistent with the higher stability and volatility of the sulphide compound relative to that of Zn

Step 2: Quantitative estimation of the extent of Cd deportment under moderately oxidising conditions

- Deportment of Cd to the vapour phase is predicted to be higher than that occurring under highly oxidising conditions, and higher than that for Zn, viz approximately > 65%
- Deportment of Cd to the matte phase is expected to be only partial, and similar to or slightly lower than that occurring under highly oxidising conditions, viz approximately 10-20%
- Deportment of Cd to the slag is expected to be lower than that occurring under highly oxidising conditions, and lower than that for Zn, viz <10%

"The modern-day approach to the problem also calls for substantial supplements to the traditional description of mineral reserves from a purely geological or process viewpoint" Rubenstein and Barsky (2002) on the problems of mineral resources development.

6

Predicting the Chemical Compositions of Copper Sulphide Ores, Flotation Tailings & Concentrates: Case Study 1

Thus far, the thesis has developed criteria, protocols and technical guidelines for predicting the distribution behaviours and deportment of elements during the formation and beneficiation of ore deposits and, ultimately disposal of solid waste outputs. The following three chapters (6-8) will demonstrate the application of the generalised methodologies and criteria developed in the previous chapters to the primary copper production industry.

Approximately 90% of the world's primary 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 copper prior to metallurgical extraction (Ayres et al, 2002; Gordon, 2002). A generalised flow-sheet depicting the mining, technically viable routes and related primary unit operations for the processing of run-of-mine copper sulphide ores is presented in Figure 6.1. In many operations, optimum copper production will probably be best achieved by using a combination of the above-mentioned processing routes. In particular, in many cases optimum economic recovery of copper from an ore deposit will require sending high grade ores (> 0.25% Cu) to milling/concentration/metallurgical extraction, low-grade ores (~ 0.25% Cu) to heap leaching and waste rock (<0.25% Cu) to dump leaching (Biswas & Davenport, 1994).

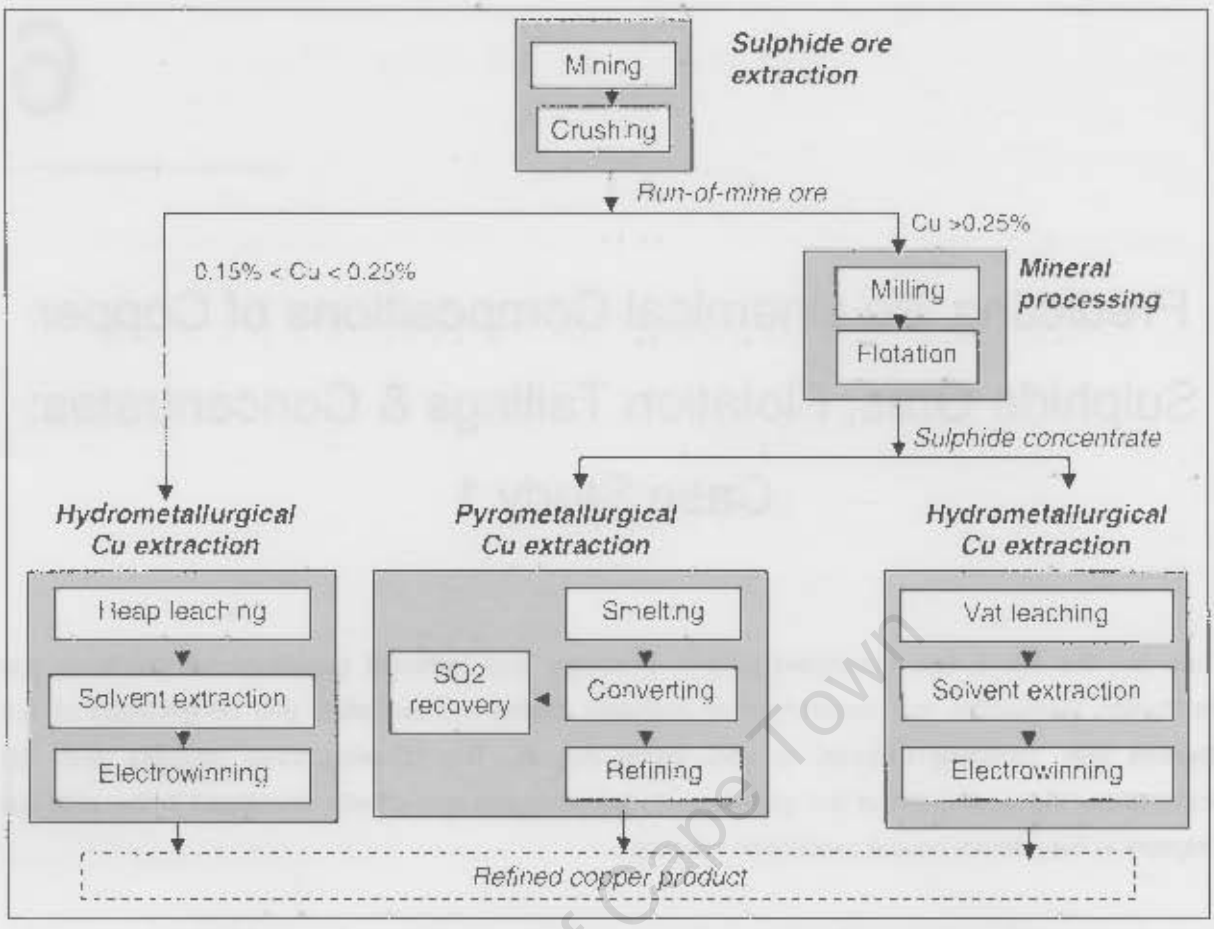


Figure 6.1: Mining and beneficiation of copper sulphide ore deposits (Biswas & Davenport, 1994)

Although a number of hydrometallurgical and biohydrometallurgical processes have been developed for the treatment of copper sulphide concentrates on a laboratory and/or pilot scale, commercial metallurgical extraction of copper from sulphide concentrates is almost exclusively conducted by pyrometallurgical means. The pyrometallurgical processing of copper sulphide concentrates entails smelting with a siliceous flux to produce a sulphide matte rich in copper, followed by subsequent conversion of the matte to a crude molten metallic blister copper containing 98 to 99 % copper. The blister copper is typically fire-refined in an anode furnace, cast into anodes and subjected to electrolytic refining to produce a high purity copper cathode, containing less than 20 ppm impurities. The conventional mining → concentration → pyrometallurgical extraction → refining process route for primary copper production is demonstrated diagrammatically in Figure 6.2.

Apart from copper, the conventional pyrometallurgical processing route frequently recovers a number of other co-elements as by-products, including sulphuric acid, arsenic, selenium, tellurium, the precious metals, molybdenum, lead, zinc and nickel (Ayres, 2002; Biswas & Davenport, 1994; Ripley et al, 1996). 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). Although the majority of the by-product recovery is from anode slimes and electrolyte bleed streams emitted from the refining operations, recovery of by-products from pyrometallurgical outputs such as furnaces flue dusts and acid plant blow down is becoming increasingly common.

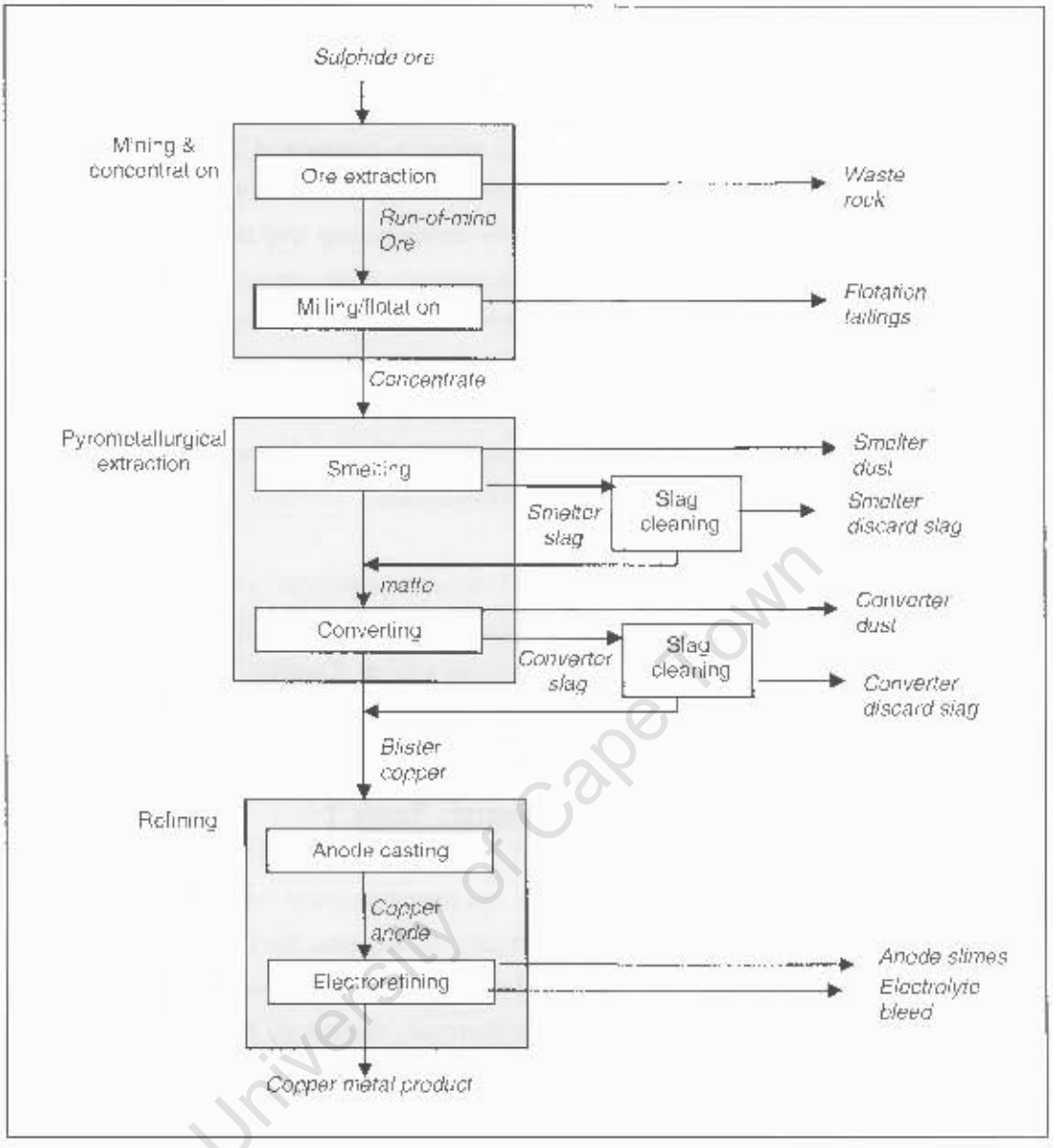


Figure 6.2: Conventional process flowsheet for primary copper production

A comprehensive survey of the published literature, as well as discussions with certain industrial organisations, has however indicated that available data and information on the deportment of minor and trace elements is extremely limited, particularly in the case of 'early' beneficiation streams (run-of-mine ore, waste rock and concentration tailings), and the list of well-known co-elements by no means complete. Even in the cases where reported data is relatively extensive, this is extremely diverse, with a large range of values being reported. These results, as summarised in Appendix 6.1, are consistent with the findings of other researchers such as Ayres et al (2002) and Stewart (2001)- i.e. currently available data pertaining to primary metal processes is incomplete, inconsistent and very uneven (see discussions in Section 1.1, Chapter 1). It is some of these data gaps and inconsistencies that the case studies in Chapters 6 to 8 will be attempting to address, through the application of the generalised methodology developed within the preceding chapters.

This particular chapter is concerned mainly with the compositions of typical copper sulphide ore deposits, containing a grade of > 0.25%, and the subsequent distribution, concentrations and mass flows of ore components during mining and concentration. In accordance with the methodological guidelines and procedural frameworks developed in previous chapters of the thesis, currently available data pertaining to the characteristics of the feed ore as well as the subsequent distribution, concentrations and mass flows of ore components during milling and flotation is first collected and reviewed (Section 6.1). This is followed by an assessment of the chemical properties and potential distribution behaviours and associations of elements during ore formation and beneficiation, on the basis of fundamental chemical and thermodynamic principles (Section 6.2). Finally, the empirical data and theoretical knowledge gained through these studies is reconciled in Section 6.3, ultimately resulting in a comprehensive list of potential distribution factors, element concentrations and their speciation in typical copper sulphide ores, flotation tailings and concentrates.

The predicted concentrations and forms of constituent elements in the flotation tailings and concentrates will, in turn, play a key role in the subsequent assessment of the chemical behaviour and element distribution profiles during land disposal of the tailings (Chapter 7) and concentrate smelting (Chapter 8).

6.1 System review and assessment: Task 1

In accordance with the discussions in Chapter 5, 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. Available data pertaining to the input and output streams over the entire ore-to-metal flowsheet is presented in Appendix 6.1. This section of the thesis summarises and reviews the available data and general information pertaining to the genesis and chemical properties of copper sulphide ore deposits, and the behaviour of such deposits during subsequent mining and concentration.

6.1.1 The genesis and chemical properties of copper sulphide ores

As a general group primary copper sulphide ore deposits are hydrothermal deposits 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, Na, Mg). Further information pertaining to generic hydrothermal deposits is presented in Appendix 3.1 of Chapter 3. Chalcopyrite ($CuFeS_2$) is by far the most predominant copper mineral accounting for ½

the world's, 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 common 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, $CuSO_4.2Cu(OH)_2$ and 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, PGMs), antimony, cobalt, nickel, tin, cadmium and molybdenum (Ayres, 2002; Biswas & Davenport, 1994; Ripley et al, 1996). Discussions in the previous section have, however, indicated that this list is by no means complete, with a typical copper deposit containing in excess of 30 elements in measurable quantities. Furthermore, whilst some of these co-elements are recovered as by-products, many of the elements occurring in copper ore deposits either deport to waste outputs or are continuously recycled, remaining locked within beneficiation circuits.

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. Appendix 6.2 summarises available data and information pertaining to the characteristics of the main classes of copper sulphide ore deposits as reported in the open literature (see for example Batty, 1981; Correns, 1969; Cox & Singer, 2003; Cox et al, 2003; du Bray, 1996; Ďuďa & Rejl, 1986; Mining Journal editorial, 1995; Seal & Foley, 2002).

The characteristics defining the various copper sulphide deposit classes are not always clear, and classification from an environmental signature point-of view is limited to relatively general criteria, such as the nature and relative quantities of sulphide and non-sulphide, or host rock, minerals.(du Bray,

1996; Seal & Foley, 2002). As indicated in Figure 6.3, the drainage chemistry at a copper mine can be expected to vary according to the following characteristics:

- ***Total sulphide mineral content:*** Ore deposits can be massive (domination of sulphide minerals, > 50%, particularly pyrite) or disseminated (with the domination of non-sulphide minerals over sulphide minerals).
- ***The base-metal content:*** Ore deposits can be simple (monometallic), with copper as the only major base metal, or complex (polymetallic) with major quantities of copper co-existing with Pb and Zn.
- ***Acid-generating and/or consuming properties of the host rock:*** The non-sulphide host rock can be comprised mainly of carbonate minerals (high acid neutralising capacity) or silicate minerals (low acid neutralising capacity).

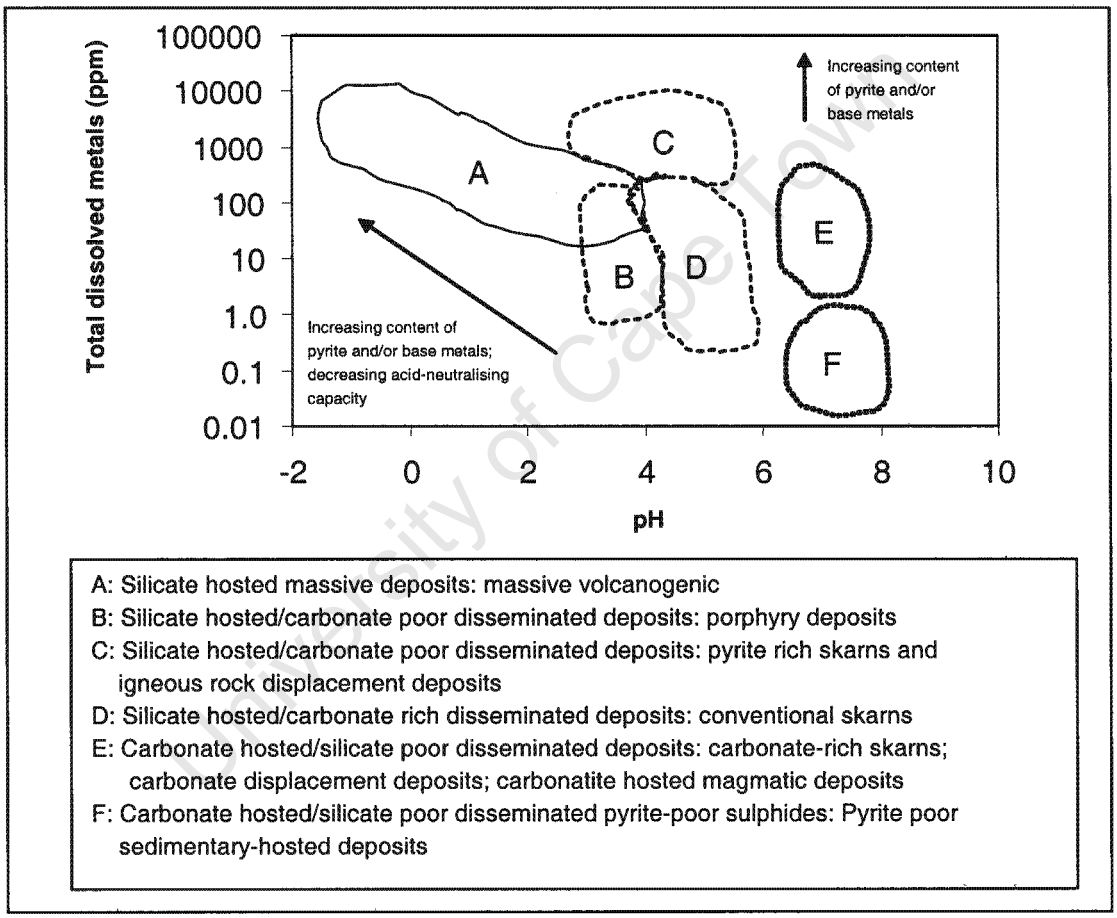


Figure 6.3: Mine water chemistry as a function of copper ore deposit characteristics (modified from du Bray, 1996; Seal & Foley, 2002)

This case study is particularly concerned with porphyry-type deposits i.e. silicate-rich, carbonate-poor disseminated deposits generally containing < 20% sulphide minerals, the majority of which are in the form of pyrite and chalcopyrite. 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).

6.1.2 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 6.4.

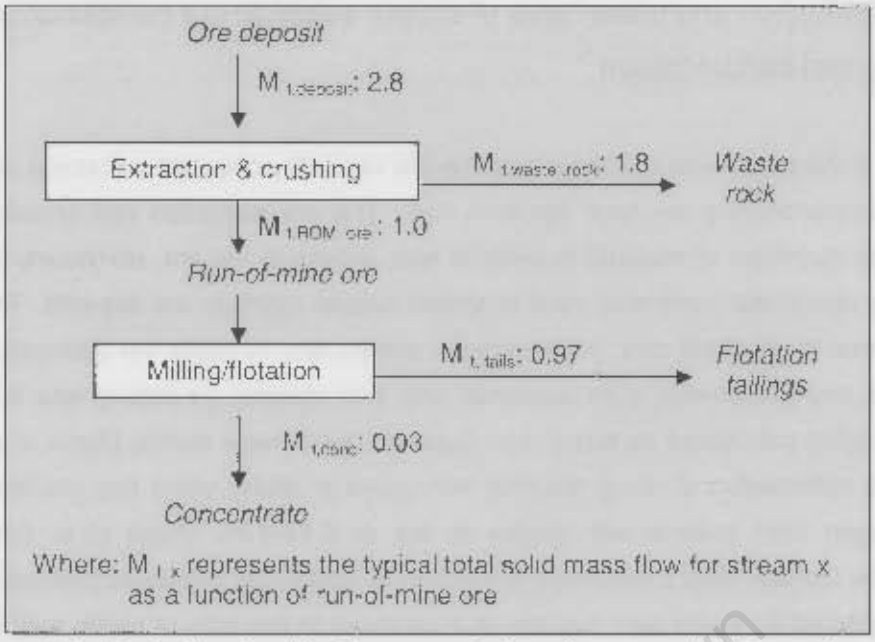


Figure 6.4: Simple flowsheet for the concentration of copper sulphide ore deposits

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 (5-15%), 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 (5-15%), 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 6.1.

The summary in Appendix 6.1 indicates that the deportment of ore components during flotation of copper sulphide ores can give rise to concentrates with a wide range of chemical and mineralogical compositions. Nevertheless, according to Ayres et al (2002) and Gordon (2002), copper sulphide concentrates will typically contain 23-27% Cu, 29-31% Fe and 30-32% S as the major components. Sulphur/copper mass ratios are generally in the order of 1.2/1, with sulphur occurring in the form of both copper sulphide (predominantly chalcopyrite, bornite and chalcocite) and iron sulphide (predominantly pyrite) minerals (Ayres et al, 2002). The remaining 10-16% of the concentrate is typically comprised of lithophilic gangue elements and other trace to moderately abundant sulphides (Ayres et al, 2002). Available results indicate, furthermore, that the sulphide ore minerals (including phases of chalcophilic and siderophilic elements) can typically vary between 2 and 8 percent, with the lithophilic gangue component being comprised mainly of silicate and, to a lesser extent, carbonate (≤ 4%) minerals.

Table 6.1: 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

6.2 Theoretical assessment of element deportment during copper sulphide ore formation and concentration: Task 2

The second task in the proposed predictive methodology (see Figure 5.1 of Chapter 5) entails a theoretical assessment of the potential element distribution behaviours and associations, in accordance with the fundamental criteria developed in Chapters 3 (for ore formation) and Chapter 4 (for ore beneficiation) of the thesis.

6.2.1 Element distributions and associations during formation of copper sulphide ore deposits.

As discussed in Chapter 3, 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 3 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. On the basis of these considerations, paragenetic elements occurring within copper sulphide ore deposits have been sub-divided into three main groups or classes:

1. ***Chalcophilic and siderophilic co-elements:*** Copper is one of a number of chalcophilic elements, which include those comprising weakly electropositive metals and semi-metals (or metalloids) with a strong affinity for "soft" sulphide-type (including selenide, telluride, arsenide and antimonide) ligands. In terms of average abundance, the majority of the chalcophilic elements are relatively scarce and, as a general group, comprise only 0.25 % of the earth's crust (Rubenstein & Barsky, 2002). Significant concentrations of chalcophilic elements generally only occur within economically viable monometallic or polymetallic sulphide deposits of the more abundant chalcophilic elements, commonly termed base metals (copper, zinc and/or lead). These deposits generally occur in association with significant quantities of iron sulphide minerals such as pyrrhotite (FeS) and, in particular, pyrite (FeS_2), which are by far the most abundant and wide-spread of the sulphide minerals within the earth's crust. Siderophilic elements occur as native elements and/or sulphides within the earth's crust and include the platinum group metals (PGMs) and gold. These elements are commonly termed precious metals, and are generally extremely scarce, making up only 0.1% of the earth's crust (Rubenstein & Barsky, 2002). Siderophilic elements have an extremely low affinity for oxygen and are almost always associated with sulphide minerals. As discussed in Chapter 3, elements in this group can exist either as dispersed elements, occurring in the structures of other more abundant sulphide minerals, particularly pyrite, or as discrete sulphide minerals. Reported and predicted associations of elements with major base metal sulphide minerals typically occurring within hypothermal sulphide deposits are summarised in Table 6.2.

   Whilst the majority of the chalcophilic and siderophilic elements falling in this group can be expected to be enriched in hydrothermal copper sulphide deposits relative to their crustal abundance, the extent to which this enrichment occurs will be dependent on the co-deposition of other major base metals (i.e. the total sulphide content and degree of polymetallic character), as well as the average crustal abundance of the individual elements. Extensive enrichment of Se and Te is suggested on the grounds that these elements are both extremely scarce within the earth's crust, and occur mainly in association with copper sulphide minerals, relative to the other base metals. Other chalcophilic elements which can be expected to be relatively highly enriched in hydrothermal copper sulphide deposits include the precious metals (PGMs, Au and Ag), Mo and As, followed by the more abundant chalcophiles of Zn and Pb. The extent to which elements commonly associated with sulphides of Zn (Ge, Cd, In), Pb (Sb, Bi, Ag, Tl and Hg), Mo (Re) and Fe (Ni, Co) are enriched will be dependent to a large extent on the distribution of these sulphides within the copper sulphide ore (i.e. polymetallic nature of the ore), as well as the thermal stability of their dominant forms. Indium (In), thallium (Tl) and, in particular, mercury (Hg), only form stable solid phases at relatively low temperatures (i.e. in the epithermal temperature range) and are thus less likely to be associated with the relatively stable chalcopyrite mineral than other chalcophilic and siderophilic elements.

Table 6.2: Predicted and reported associations of chalcophiles and siderophiles with major base metal sulphide phases

Base metal sulphide	Reported associations (after Ayres et al, 2002; Benzaazoua et al 2002; Cox, 1995; Hayes, 1985; Ripley et al, 1996; Rubenstein & Barsky, 2002; Seal & Foley, 2002).	Predicted associations	
		On the basis of similarities in ionic radii	On the basis of similarities in crystallisation temperatures
Sphalerite (ZnS)	*Cd* (0.5-1), *In* (1%), Ga (<0.l), Tl (up to 40 ppm), *Ge* (<0.3), Ag, Cu (0.26%), Se, *Pb*	Fe(II), Ni(II), Co(II), Cu(II), As(III), *In (III)*, Mo(IV)-Re(IV)	As, Au, Fe, Cu, *Pb*, Ag, Bi, Se Te.
Galena (PbS)	Cd, *Tl*, Se, Te, *Bi, Ag*, Sb, Mn, *Zn*	*Bi(III)*, Hg(II), *Ag(I)*, Au(I)	As, Au, Fe, Cu, *Zn, Ag, Bi*, Se, Te
Chalcopyrite ($CuFeS_2$)	Cd, In (1%), *Se, Te*, Re, Pd, Pt, P, Ir, Ru, Os, Bi, *Mo, As,* Co. Ge, Ga, Sn, Pb, Zn, Tl, Ag, *Au*	Fe(II), Ni(II) - Co(II), Zn(II), *As(III)*, In (III), *Mo(IV)-Re(IV)*	*Fe,* Pb, Zn, Au, Ag, As, Bi, *Mo, Se, Te*
Pyrite (FeS_2)	*As* (up to 7%), Hg, Se, Tl, Cu, Pb (up to 0.6%), *Co* (up to 3%), *Ni* (up to 9.6%), Cd , Zn	Cu(II), *Ni(II)-Co(II)*, Zn(II), As(III), In (III), *Mo(IV)-Re(IV)*	Pb, Zn, Cu, Au, Ag, *As*, Bi, Mo, Sb, Hg, Se, Te.
Where elements in italics correspond to those which are generally considered to be commonly occurring co-elements			

2. ***Accessory lithophilic co-elements commonly associated with post-magmatic, hydrothermal deposits:*** The lithophilic elements, occurring mainly as oxides (including simple oxides as well as complex oxides, such as carbonates and silicates) can be divided further into two sub-groups, viz. the major rock-forming lithophilic elements of Si, Al, Fe, Ca, K, Na and Mg which make up the bulk of the earth's crust, and the remaining lithophilic elements which are widely distributed as accessory minerals, occasionally occurring as local ore enrichments. As discussed in Chapter 3, lithophilic elements of relatively high charge density form oxides with relatively low melting points which, like the chalcophiles, crystallise from magmatic fluids in the hypothermal, and even mesothermal, post-magmatic temperature ranges. Such compounds include the relatively insoluble alkaline earth metal (mainly Ca and Ba) compounds with oxyanions (tungstate, borate, phosphate, sulphate and carbonate) and fluoride, as well as quartz, Sn(IV) oxide and elements such as Co, Ni and Ga which can occur as both sulphides and oxides within the earth's crust. Many of these elements (particularly Si, Ca, Mg) are abundant throughout the earth's crust, and hence, whilst they may occur in significant quantities within hydrothermal sulphide deposits, are unlikely to be significantly enriched relative to their crustal abundance. Notable exceptions are tungsten (W), tin (Sn) and boron (B) which are less abundantly distributed, and thus likely to occur in local hydrothermal deposits in significantly elevated quantities.

3. ***Major host rock-forming and magmatic accessory minerals:*** Hydrothermal deposits typically occur as veins within and/or are closely associated with late magmatic stage host rocks and their alteration products, particularly granitic igneous rock and granitic pegmatites (rich in Si, Al and K and depleted in Mg and Fe); intermediate alkaline (rich in alkali metals) and/or calc-alkaline (Ca enriched) rocks. Sulphide mineral deposits are also known to be associated with carbonate minerals in sedimentary limestone deposits. As discussed in Chapter 3 these rocks will also contain a number of accessory minerals with similar thermal properties to the major rock-forming minerals. In particular, granite pegmatites, which are coarse-grained irregular silicate vein-like deposits precipitating from silica rich aqueous solution in the final stages of magma consolidation, frequently contain economically significant concentrations of accessory minerals and associated elements, including Be, Zr, Hf, Ta, Nb, REE (rare earth elements), U and Th. Although most of the elements occurring in this group, particularly the major rock-forming mineral elements, are likely to be associated with hydrothermal sulphide deposits to a significant extent, enrichment relative to their average crustal abundance is not expected to be significant.

6.2.2 Element distributions and associations during concentration of copper sulphide ore deposits

As discussed in Chapter 4, the milling and flotation of run-of-mine copper ores entails size reduction and separation of mineral phases by physical means, and for the most part does not result in chemical changes to the mineral component of the ore. Deportment of minor and trace elements to the tailings will thus be largely dependent on their mineralogy, particularly speciation and mode of occurrence, in the sulphide ore body (Hayes, 1985; Wills, 1997). 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 concentrations within ore deposits will be largely dependent on the ratios of the major minerals with which they are associated.

In terms of deportment behaviour during concentration, the mineral and associated elements within a typical copper sulphide run-of-mine ore can thus be divided into the following main groups:

- Copper sulphide ore minerals (mainly chalcopyrite, and, to lesser extent bornite and chalcocite)
- Iron sulphide ore minerals (mainly pyrite)
- Minor to trace sulphide ore minerals, comprising the chalcophilic and siderophilic co-elements
- Silicate (mainly K-Al silicates and quartz), carbonate (mainly calcite) and oxide (mainly iron and tin oxides) gangue minerals

6.3 Mass balance calculations and data reconciliation: Task 3

As discussed in Chapter 4, the distribution behaviour of the targeted metal and major ore components is generally fairly well understood, and data gaps and inconsistencies pertaining to the main mineral groups and their major element components during mining and concentration of copper sulphide ore deposits can thus be addressed on the basis of available data and information through the application of meaningful generalisations and simple mass balance calculations. In contrast, the distribution behaviour of many of the trace and minor elements during ore formation and processing is generally poorly understood. In accordance with the technical guidelines outlined in Chapter 5 , the derivation of distribution and process inventory data pertaining to these elements will require reconciliation of the available historical empirical data (Section 6.1) with a fundamental understanding of their chemical behaviour during the formation, mining and concentration of the copper sulphide ore deposit (Section 6.2). The generic protocol presented in Chapter 4 (Figure 4.3) for predicting the chemical characteristics of ore deposits and beneficiation streams has been adapted to this particular case study in Figure 6.5.

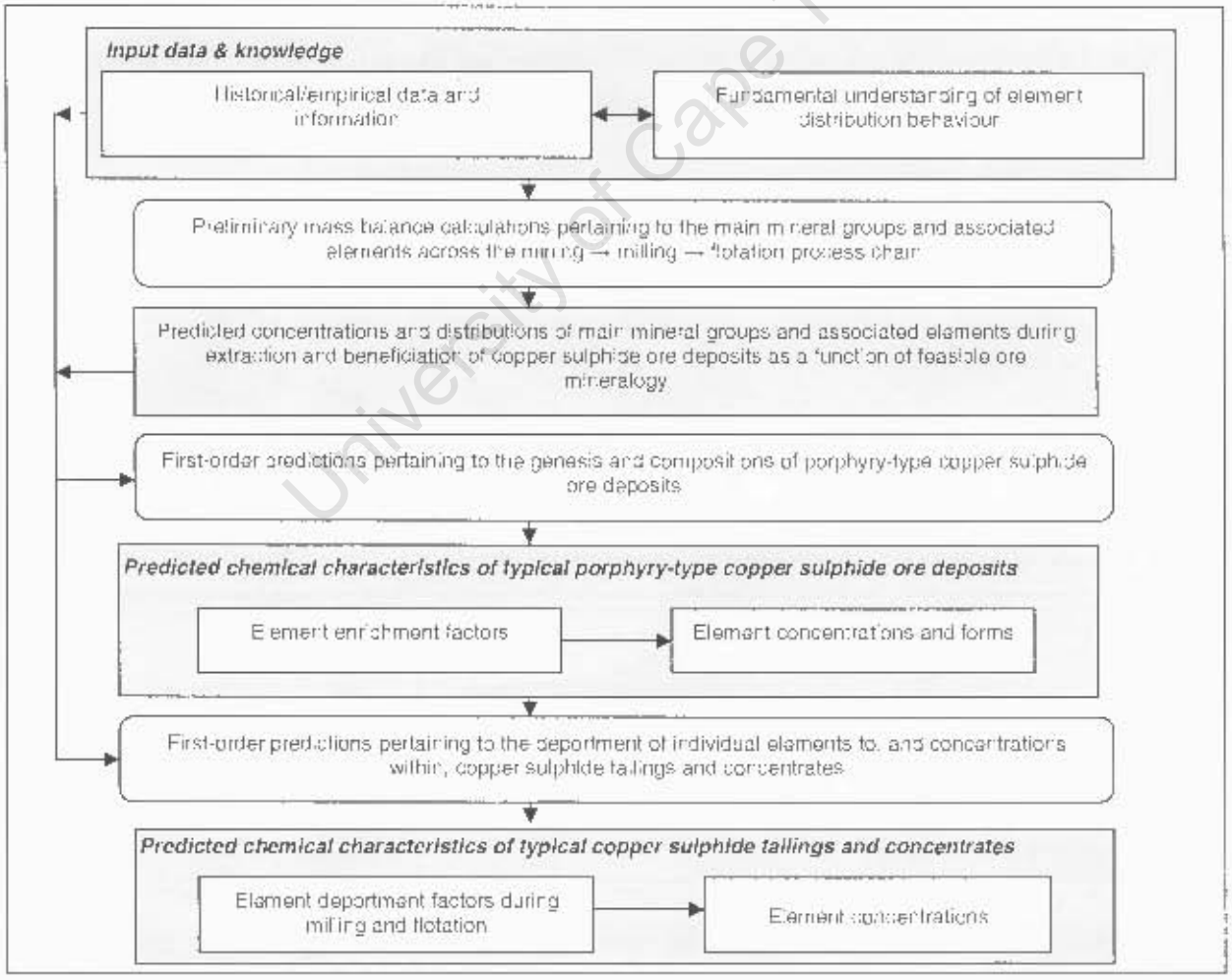


Figure 6.5: Detailed procedural framework for predicting the chemical characteristics of copper sulphide ore deposits, flotation tailings and concentrates.

In accordance with this framework, mass balance calculations pertaining to the main mineral groups and associated elements during the extraction and concentration of porphyry-type copper sulphide ore deposits are presented in Section 6.3.1. Section 6.3.2 is concerned with the derivation of a comprehensive list of potential element distribution factors and concentration ranges, through the reconciliation of available empirical and theoretical information generated in the previous sections of this chapter.

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

The review in Section 6.1 indicated that the concentrate output streams are relatively well characterised in comparison with the other early beneficiation streams (run-of-mine ores, waste rock and tailings). Nevertheless, the mass balance calculations summarised in Table 6.3 indicate that the "typical" concentrations of the major elements (Cu, Fe and S) and sulphur/copper mass ratios, as reported by Ayres et al (2002) and Gordon (2002), can correspond to a relatively diverse range of mineral compositions- the pyrite/copper mineral mass ratios typically varying from approximately 0.1/1 to 0.8/1.

Table 6.3: Predicted concentrations of the main mineral groups and associated elements in typical copper sulphide concentrates

Component	Component values				
Major sulphide ore minerals (kg/t)					
Chalcopyrite	700	550	450	370	200
Bornite	10	80	40	80	80
Chalcocite	10	10	90	90	180
Total copper sulphide minerals	720	640	580	540	460
Pyrite	100	150	200	230	350
Total	820	790	780	770	810
Major gangue minerals (kg/t)	100-160	130-190	140-200	150-210	110-170
Trace-minor sulphide ore minerals (kg/t)	20-80	20-80	20-80	20-80	20-80
Major sulphide ore elements (kg/t)					
Copper	259	252	256	266	266
Iron	307	289	276	269	274
Sulphur	318	310	308	306	330
Mass ratios (t/t)					
S/Cu	1.2	1.2	1.2	1.2	1.2
Pyrite/copper sulphide minerals	0.14	0.23	0.34	0.43	0.76

Mass balance calculations pertaining to the concentrations and distributions of the main mineral groups and associated elements during mining and concentration of copper sulphide ore deposits, as a function of iron sulphide/copper sulphide mineral ratios in the concentrate, are presented in Table 6.4. Detailed mass balance calculations and assumptions are presented in Appendix 6.3.

Table 6.4: 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: 0.03/1; flotation tailings/ROM ore: 0.97/1; waste rock/ROM ore: 1.8/1

tailings from milling and flotation, increases as the mass ratios of pyrite to copper sulphide minerals in the ore and concentrate increase.

6.3.2 Derivation of individual element distribution and concentration data ranges

Predicted element distribution factors

Reconciled enrichment factors for individual elements in typical porphyry copper sulphide ores, tailings and concentrate streams are summarised in Table 6.5. Detailed calculations are presented in Appendix 6.4.

Reconciliation of available quantitative data (Section 6.1.1) with the qualitative predictions (Section 6.2.1) confirms that the extent of enrichment of elements in copper sulphide ores is highly dependent on both their stable forms under the high temperature reducing conditions corresponding to the formation of hypo- to meso- hydrothermal deposits, as well as their relative abundance within the earth's crust and within other base-metal deposits. As predicted, available analytical data indicates that the chalcophilic and siderophilic elements are generally enriched to a significant extent, 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. 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. The relatively extensive enrichment of arsenic and antimony in typical porphyry-type copper sulphide deposits indicates that these elements are likely to be present as the more thermally stable forms of arsenopyrite (FeAsS) and tetrahedrite ($(CuFe)_{12}Sb_4S_{13}$) respectively. Available analytical results also confirm that the only lithophilic elements which are consistently 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.

Potential element distributions during subsequent milling and flotation of the porphyry-type ROM ores have been predicted by reconciling available empirical deportment data (Section 6.1.2); an understanding of the forms of the elements within typical porphyry-type copper sulphide ore deposits and the distribution behaviour of such during flotation (Section 6.2.2); and the results of the mass balance calculations pertaining to the concentrations and distributions of major mineral groups and associated elements (Section 6.3.1). 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

Subsequent calculation of the extents to which elements are enriched in the tailings relative to their average crustal abundance (see Table 6.5) indicate that the enrichment of lithophilic gangue elements in the tailings 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. Whilst iron and sulphur deport to the tailings output stream to a significant extent (> 60%) during flotation of the run-of-mine ore, the other chalcophilic and siderophilic elements report to the tailings only partially (< 30%). However, although depleted relative to the parent ore, many of these elements, particularly the scare to trace elements, may still be highly enriched in the tailings relative to their average crustal abundance. In such cases this could have significant consequences in terms of environmental impact (e.g. arsenic and cadmium), as well as losses in potentially valuable metal resources (e.g. precious metals).

The results in Table 6.5 also indicate that the lithophilic elements are generally depleted in the concentrate output stream relative to their average crustal abundance, with only B, Sn and W likely to be enriched to any significant extent. In contrast, many of the scarce to trace chalcophilic and siderophilic elements (including precious metals, As, Sb, Bi, Cd, Re & Mo and, in particular, Se and Te) are likely to be enriched to a significant extent in copper sulphide concentrates, in some cases to an even greater extent than copper. This can be attributed to a combination of high enrichment in typical copper sulphide ores, as well as extensive deportment to the concentrate output stream during subsequent beneficiation (> 30%). Other chalcophiles which may be enriched to a significant extent in these concentrates include Zn, Pb, In, Tl, Hg, Ge and, to a lesser extent, Ni and Co.

Table 6.5: Predicted enrichment factors for elements in typical porphyry-type copper sulphide ores, tailings and concentrates

Group description	Relative natural abundance	Elements	Enrichment factors[1]		
			Ore	Tailings[2]	Concentrate[2]
I: Chalcophiles and siderophiles					
IA Hypothermal to mesothermal elements associated mainly with copper sulphide ores	Scarce	Te-Se	100-1000	10-300	3000-34000
	Minor	Cu	100-200	15-25	4500-5000
	Moderately abundant	S	50-200	20-200	400-600
IB: Hypothermal to mesothermal elements associated with copper and/or other sulphide ores	Scarce-trace	PGMs-Ag-Au, As-Sb-Bi, Cd, Re-Mo	10-1000	1-300	250-34000
	Minor	Zn- Pb	2-20	0.2-6	50-700
	Major	Fe	0.2-2	0.2-2	3-6
IC: Elements occurring mainly as epithermal, volatile minerals	Scarce	In-Tl-Hg	2-20	0.2-6	50-700
II Intermediate elements					
Elements occurring as sulphide as well as oxides in natural environments	Trace	Ge	2-20	0.2-6	50-700
	Minor	Ni-Co	0.1-2	<1	3-70
III: Lithophilic elements					
IIIA: Elements mainly associated with post-magmatic hydrothermal deposits	Trace	B-Sn-W	5-100	5-100	0.6-25
	Moderately abundant	P	0.1-5	0.1-5	0.01-1
IIIB: elements commonly occurring as accessory minerals in acid and pegmatitic type rocks (late magmatic deposits)	Scarce -minor	Ta-Nb-REE-Be-Hf, Li, Br, I	0.1-10	0.1-10	0.01-2
	Moderately abundant	F-Cl, Rb, Zr	0.1-5	0.1-5	0.01-1
IIIC: elements commonly occurring as accessory minerals in basic and ultrabasic rocks	Trace-minor	Sc, Ga, U	0.1-5	0.1-5	0.01-1
	Moderately abundant	Ba-Sr, V-Cr-Ti-Mn	0.1-2	0.1-2	0.01-0.5
IIID: major rock-forming lithophilic elements	Major	Si, Al, K-Na, Mg-Ca	0.1-1.2	0.1-1.2	0.01-0.3

(1) Relative to average crustal abundance : Scarce elements: ≤ 1ppm; trace elements: 1< ppm ≤ 10; minor elements: 10< ppm < 100; moderately abundant elements: 100 ≤ ppm<10 000; major elements > 10 0000

(2) Based on tailings/ore mass distribution ratios: 0.994-0.997 for lithophilic gangue elements; 0.1-0.15 for copper; 0.59-0.93 for Fe and S; 0.1-0.3 for other sulphide-associated (chalcophilic and siderophilic) elements

- **Predicted element concentration ranges**

Predicted data pertaining to the concentrations of elements in porphyry-type copper sulphide ores, tailings and concentrates is presented in Table 6.6. Calculations are detailed in Appendix 6.4.

Table 6.6: Predicted element concentration ranges for porphyry-type copper sulphide ores, tailings and concentrates

Sulphide ore-forming elements				Lithophilic gangue-forming elements			
Element	Ore	Tailings	Concentrate	Element	Ore	Tailings	Concentrate
Major ore elements (%)							
Cu	0.5-1.0	0.08-0.13	25-30	Si	21-34	21-35	2.5-8
Fe	1-10	0.8-9.5	15-30	Al	4-10	4-10	0.5-2.2
S	2-11	1.0-11	20-30	Mg	0.2-3	0.2-2.6	0.02-0.6
				K	0.3-3.4	0.3-3.5	0.03-0.8
				Ca	0.4-4	0.4-4.5	0.05-1.0
				Na	0.3-3	0.3-3.2	0.03-0.7
Moderately abundant ore elements (ppm)							
Zn	150-1600	15-500	4000-55000	Ti	450-9000	400-9000	50-2000
Pb	30-300	5-100	800-11000	P	100-6000	100-6100	15-1400
As	5-1800	2-550	100-62000	F	60-3000	60-3000	7-680
Mo	15-1500	2-450	400-50000	Mn	100-2000	100-2000	11-450
Bi	2-200	0.2-60	50-7000	B	50-1000	50-1000	5-230
Sb	2-200	0.2-60	50-6840	Ba	40-860	45-880	5-200
Cd	2-200	0.2-60	50-6840	REE	10-850	10-870	1-190
Ni	8-150	1-50	200-5000	Sr	30-600	30-600	3-130
Se	10-100	1-30	300-3000	Rb	10-600	10-600	1-140
				Zr	10-500	50-500	1-110
				Cl	10-500	50-500	1-110
				V	15-300	15-300	2-70
				Li	5-300	15-300	0.5-70
				Sn	15-300	15-300	2-70
				Cr	10-200	10-200	1-50
				Nb	2-200	10-200	0.1-40
				W	5-100	5-100	0.5-20
Minor ore elements (ppm)							
Ag	1.0-70	0.1-20	20-2500	Ga	2-80	2-80	0.1-15
Co	2.5-50	0.3-15	70-1700	Sc	1-70	1-70	0.1-15
Ge	2-20	0.5-10	80-1000	Be	0.5-30	1-30	0.2-5
				Hf	0.5-25	0.5-30	<0.1-5
				Br	0.5-25	0.5-30	<0.1-5
Trace ore elements (ppm)							
Tl	0.6-6	0.06-2	15-200	U	<1-10	1-10	0.1-2
Pt	0.05-5	0.01-2	1-170	Ta	<1-10	0.1-10	0.01-2
Au	0.04-4	0.002-1	1-140	I	<1-5	0.05-5	<0.01-1
Pd	0.1-2	0.01-3	3-350				
Hg	0.2-1.5	0.02-0.5	5-70				
Scarce ore elements (ppm)							
Te	0.1-1.0	0.01-0.5	3-30				
In	0.1-1	0.01-0.5	3-50				
Re	0.01-1	<0.01-0.5	0.5-30				

Detailed predictions indicate that the concentrations of lithophilic gangue elements as well as Fe and S in the tailings are similar to the concentration levels in the parent ore, whilst the concentrations of other chalcophiles and siderophiles are generally lower. In the case of concentrates, the concentrations of lithophilic gangue elements are generally considerably lower, and those of the chalcophiles and siderophiles much higher, than the concentrations levels in the parent ore.

Predicted data relating to mineralogical compositions of typical porphyry copper sulphide ores, tailings and concentrates is summarised in Table 6.7. Details pertaining to element speciation in these input-output streams are presented in Appendix 6.4.

6.4 Summary and concluding remarks

The specific aim of this chapter was to demonstrate application of the generalised methodologies and criteria developed within the preceding chapters of the thesis in terms of addressing current data gaps and inconsistencies pertaining to the compositions of early beneficiation input-output streams associated with the primary copper industry. This entailed the generation of a comprehensive inventory list of trace, minor and major elements across the ore→milling→flotation processing chain, through reconciliation of available historical data with a fundamental understanding of the factors influencing element properties and chemical distribution behaviours during the formation, extraction and flotation of generic porphyry-type copper sulphide ore deposits.

Whilst the predicted inventory lists are considerably more complete and less dispersed than those compiled on the basis of available historical data alone, predicted element concentration ranges for the generic porphyry-type copper sulphide run-of-mine ores, tailings and concentrates remain relatively broad. This can be attributed mainly to the large number of site-specific factors (including local geology, hydrology and climatology) influencing the deportment of elements to, and concentrations within, such deposits. Significant differences in terms of element enrichment factors and concentration levels can thus occur within deposits arising from different environmental regions (and even within different zones of the same deposit), resulting in relatively high levels of uncertainty pertaining to generic data on mineral deposits, and consequently in the streams arising from the beneficiation thereof. An improved quantitative understanding of the relationship between the chemical characteristics of ore deposits and their genesis will greatly improve the quality of feed-forward predictions of process inventory streams, such as that conducted within this chapter. Recent years have seen the development of a number of advanced methods, including the JKTech's Mineral Liberation Analyser (MLA)[9] and Intellection/CSIRO's QEMSCAN™ analyser[10], for the quantitative mineralogical analysis of complex ore bodies, as well as a number of research initiatives focusing on the improved understanding of the genesis of ore bodies and the fundamental relationships between ore characteristics and subsequent beneficiation processes (see for example current research

[9] Julius Kruttschnitt Mineral Reseach Centre (www.jktech.com.au)

[10] Intellection-CSIRO (www.csiro.au)

initiatives by the ARC Centre of Excellence in Ore Deposits[11] at the University of Tasmania). A recent "school" held by the South African Institute of Mining and Metallurgy (2005) has, however, indicated that current studies on ore deposits are still concerned primarily with techno-economic optimisation of ore processing operations, with virtually no links being made between ore characteristics and environmental performance.

Nevertheless, the generic case study conducted in this chapter provided data of key significance in terms of early stage decision-making, as well as further data collection and risk assessment studies in later design stages. In particular, the generic predictions have indicated that a number of the chalcophilic co-elements (i.e. elements commonly occurring as sulphide 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) are enriched to a significant extent relative to their average crustal abundance in copper sulphide ore deposits, some to an even greater extent than the targeted copper metal. As indicated in Chapter 2 of the thesis, many of these chalcophilic elements are highly to acutely toxic (As, Cd, Sb, Se and Te), whilst the siderophilic elements are generally of high economic value. Subsequent deportment of these elements to tailings and/or concentrate outputs can have significant implications in terms of environmental impact, as well as losses in potentially valuable metal resources.

Elements in the copper sulphide tailings output stream are screened and ranked in accordance with their relative environmental significance in Chapter 7 of the thesis. Chapter 8 investigates the potential distributions of constituents within the concentrate output stream during subsequent smelting operations.

[11] www.codes.utas.edu.au

Table 6.7: 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	

Appendix 6.1: Available data pertaining to input-output streams associated with the mining and beneficiation of copper sulphide ores

Mining and concentration streams: Element concentrations

Component	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

Mining and concentration streams: Mineral concentrations

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]

Pyrometallurgical process stream compositions

Component	Matte	Smelter dusts	Smelter slag	Blister copper	Converter dust	Converter slag
Major ore components						
Copper	350-700[4, 8,35]	5-270[1,4,19,20,23]	4-28[1,4,8,15,21,22,34]; 240-478[1,4,8,19,21,22]	980-990[4]	40-83[15,23]	20-85[4,8,24]; 350-550[4,8,24]
Iron	100-400[4, 8,35]	38-292[1,4,19,23]	1.1-50[1,4,8,19,21,22]	0.001-3[4]	10-20[15,23]	11-49[8,24]
Sulphur	150-250[4, 8,35]	70-120[4,20,23]		0.01-12[4]	86[23]	
Minor ore components						
Arsenic	0-5[4,23,35]	11-129[1,19,20,23]	0.08-0.4[1,19,34]; 0.1-3.4[15,21,34]	0.2[4,23]	0.14-45[19,23]	0.8[23]
Lead	0-15[4,35]	2.8-445[1,19,20,23]		0-5[4]	200-300[19,23]	n/a
Molybdenum	n/a	6-16[19]	n/a	n/a	n/a	n/a
Zinc	0-10[4]	15-123[1,19,20,23]	0.5-40[1,19,21,22,34]	0[4]	100-160[19,23]	4.3-40[4,24]
Trace ore components						
Antimony	0-5[4,35]	0.2-4[1,19,20,23]	0.4-0.6[1,19,21]	0-1[4]	2[23]	n/a
Bismuth	0-1[4]	0.4-19[19,20]	n/a	0-0.3[4]	22-35[16]	n/a
Boron	n/a	n/a	n/a	n/a	n/a	n/a
Cadmium	n/a	2-8[19,20]	0.01-0.03[21,34]	n/a	10-40[15]	n/a
Chromium	n/a	n/a	0.7[34]	n/a	n/a	n/a
Cobalt	n/a	n/a	0.008-4[22]	n/a	n/a	3.6[24]
Germanium	n/a	n/a	n/a	n/a	n/a	n/a
Gold	0-0.03[4]	n/a	n/a	0-0.04[4]	n/a	n/a
Indium	n/a	n/a	n/a	n/a	n/a	n/a
Manganese	n/a	n/a	0.3-4.9[21,22]	n/a	n/a	n/a
Mercury	n/a	n/a	n/a	n/a	n/a	n/a
Nickel	7-10[35]	n/a	0.01-0.6[21,22,34]	n/a	n/a	0.45[24]
Palladium	n/a	n/a	n/a	n/a	n/a	n/a
Platinum	n/a	n/a	n/a	n/a	n/a	n/a
Phosphorous	n/a	n/a	n/a	n/a	n/a	n/a
Rhenium	n/a	0.17-0.3[20]	n/a	n/a	n/a	n/a
Selenium	n/a	n/a	n/a	n/a	n/a	n/a
Tellurium	n/a	n/a	trace[21]	n/a	n/a	n/a
Thallium	n/a	n/a	n/a	n/a	n/a	n/a
Silver	0-3[4]	0.16[20]	n/a	0-5[4]	n/a	n/a
Tin	n/a	0.2[23]	n/a	n/a	7[23]	n/a
Titanium	n/a	n/a	n/a	n/a	n/a	n/a
Tungsten	n/a	n/a	n/a	n/a	n/a	n/a
Vanadium	n/a	n/a	n/a	n/a	n/a	n/a
Zircon	n/a	n/a	n/a	n/a	n/a	n/a
Major/minor gangue						
Aluminium	n/a	5-20[4]	10-83[4,19,21,22]	n/a	n/a	0-28[4]
Calcium	n/a	n/a	7-124[1,4,8,19,21,22]	n/a	n/a	0-140[4]
Magnesium	n/a	411[4]	0.3-14[4,21,22]	n/a	n/a	0-12[4]
Potassium	n/a	n/a	n/a	n/a	n/a	n/a
Silica	n/a	18-93[4,23]	115-191[1,4,8,19,21,22]	n/a	n/a	107[8]
Sodium	n/a	n/a	n/a	n/a	n/a	n/a
Minor/trace gangue						
Barium	n/a	n/a	n/a	n/a	n/a	n/a
Chloride	n/a	n/a	n/a	n/a	n/a	n/a
Fluoride	n/a	12[20]	n/a	n/a	n/a	n/a
Strontium	n/a	n/a	n/a	n/a	n/a	n/a

Refining stream compositions

Component	Acid blowdown (kg/m^3)	Cathode copper (kg/t)	Anode slimes (kg/t)	Electrolyte bleed (kg/m^3)
Major ore components				
Copper	0.5-2.1[4,16]	995-999.95[1,4,8,25]	10-707[1,19,25,27,28-33]	26-60[4,5,7,8,20,26]
Iron	1.2[19]	0.001-0.04[1,4,8,25]	0.4-20[14,29-31,33]	0.1-10[4,5,19,25]
Sulphur	n/a	0.004-0.03[1,4,8,25]	17-72[1,25,33]	n/a
Minor ore components				
Arsenic	0.14-5[4,19]	0.001-0.02[1,4,8,25]	3-100[1,19,25,27,29-33]	0.8-20[4,8,19,25,26]
Lead	n/a	0.0001-0.1[1,4,8,25,26]	3-350[19,25-27,29-33]	n/a
Molybdenum	n/a	n/a	n/a	n/a
Zinc	0.5-2[4,19]	n/a	0.08-4[30,33]	0.17-0.42[13,25]
Trace ore components				
Antimony	n/a	0.001-0.03[1,4,8,25]	1-160[1,19,25,27,29-32]	0.35-0.6[4,25]
Bismuth	0.07[19]	0.0001-0.001[4,8,25]	1.6-30[19,25,27,29-33]	0.03-0.2[4,5,7,8,25,26]
Boron	n/a	n/a	n/a	n/a
Cadmium	0.4[19]	n/a	n/a	0.003[19]
Chromium	0.18[19]	n/a	n/a	n/a
Cobalt	n/a	n/a	<0.03[33]	0.053-6[19]
Germanium	n/a	n/a	n/a	n/a
Gold	n/a	0.0001[4,25]	0.5-20[19,25,27,29-33]	n/a
Indium	n/a	n/a	n/a	0.1[7,8]
Manganese	n/a	n/a	n/a	n/a
Mercury	n/a	n/a	n/a	n/a
Nickel	0.25[19]	0.0001-0.04[1,4,8,25,27]	0.05-450[19,25,27,29,31,33]	n/a
Palladium	n/a	n/a	0.06-2[19,30]	n/a
Platinum	n/a	n/a	0.001-0.5[19,30]	n/a
Phosphorous	n/a	n/a	n/a	n/a
Rhenium	n/a	n/a	n/a	n/a
Selenium	n/a	0.0001-0.004[4,25]	5-580[19,25,27,29-33]	0.004[19]
Tellurium	n/a	0.0001-0.0015[4,25]	5-206[19,25,27,29-33]	0.02[19]
Thallium	n/a	n/a	10-336[19,25,27,29-33]	n/a
Silver	n/a	0.004-0.02[4,8,25,26]	6-90[19,30-31]	n/a
Tin	n/a	n/a	0.06[31]	n/a
Titanium	n/a	n/a	n/a	n/a
Tungsten	n/a	n/a	n/a	n/a
Vanadium	n/a	n/a	n/a	n/a
Zircon	n/a	n/a	n/a	n/a
Major/minor gangue				
Aluminium	0.04[19]	n/a	4-13[32,31,33]	0.3[25]
Calcium	n/a	n/a	0.07-22[30-31]	0.39[25]
Magnesium	n/a	n/a	0.06-2[30-31]	0.07[25]
Potassium	n/a	n/a	n/a	n/a
Silica	n/a	n/a	9-90[30,33]	n/a
Sodium	n/a	n/a	n/a	1.6[25]
Minor/trace gangue				
Barium	n/a	n/a	80[33]	n/a
Chloride	0.4-5[19]	n/a	n/a	0.02-0.06[19]
Fluoride	1-3[7,8]	n/a	n/a	n/a
Strontium	n/a	n/a	n/a	n/a

Appendix 6.2: Available data and information pertaining to copper sulphide ore deposits

General description of copper deposit classes

(after Cox & Singer, 2003; Cox et al 2003; du Bray, 1996; Mining Journal editorial, 1995; Seal & Foley, 2002)

- ***Porphyry deposits***

  Porphyry copper deposits are large, 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 occurring between 0.4% and 8%. Copper commonly occurs with molybdenum and /or gold and silver, forming porphyry Cu-Mo and Cu-Au sub-groups. Porphyry deposits 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.

- ***Copper skarns***

  These deposits are hosted by carbonate rocks such as limestones, dolostones and alkaline rocks containing calc-silicate minerals, and are frequently closely associated with other copper deposit types such as porphyry and polymetallic vein deposits. Local concentrations of ores can consist of massive concentrations (>50%) of sulphide minerals. The grades of Cu skarns are typically 2% Cu with < 1g/t Au and 10g/t Ag. Although carbonate minerals are commonly present, the relative carbonate/silicate ratios, and hence acid buffering capacity, can vary quite considerably.

- ***Polymetallic veins and replacement deposits***

  These deposits are generally small, with sulphur grades varying from disseminated to massive (>50% sulphide). The majority of the polymetallic and replacement deposits are hosted in carbonate-rich sedimentary rocks and have similar properties to copper skarns and sedimentary deposits. Deposits can, however, also be hosted by igneous rocks, particularly granitic type rocks containing quartz, chlorite and epidote minerals. Vein and replacement copper deposits make up about 7% of worldwide copper mining activity.

- ***Sedimentary deposits***

  Sedimentary deposits are comprised of beds of shale or sandstone impregnated with copper minerals. They are generally smaller than porphyry deposits, with copper grades varying between 2% and 4%. Silver and/or cobalt are sometimes produced as co-products. Whilst only accounting for about 6% of copper mining activities in the USA, sedimentary deposits make up about 24% of worldwide copper mining activity, and include the Central African copper belt.

- ***Massive volcanogenic deposits***

  Massive sulphide deposits are typified by ores that comprise greater than 50% sulphide minerals, such as pyrite, pyrrhotite, chalcopyrite, sphalerite and galena. Host rocks are typically acidic or basic volcanic rocks or silica rich sedimentary rocks. Carbonate minerals are typically absent or

are a minor component of host rocks. These massive sulphide deposits are commonly associated with regionally developed iron and/or manganese rich metalliferous sediment. They are more numerous than porphyry and sedimentary-type deposits, but are smaller in capacity and reserves. These deposits make up approximately 7% of worldwide mining activity.

- ***Magmatic deposits***

  These deposits consist of massive layered or disseminated sulphides associated with igneous rock intrusions, in which the sulphides have collected by gravitational settling whilst the rock was still molten. Examples of magmatic deposits in South Africa include the ultrabasic magmatic deposits, containing significant quantities of Ni, Co and PGMs associated with chromite, and the unusual alkaline carbonatite intrusions of the Palabora district. These deposits all tend to be polymetallic, fine to ultra fine, and are frequently intergrown with large amounts of pyrite and pyrrhotite. Magmatic copper deposits make up approximately 4% of the worldwide copper mining activity (Mining Journal editorial, 1995)

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

Reported element concentrations in copper ore deposits

Element	Porphyry deposits (du Bray, 1996; Bulatovic, 1998)			Skarn deposits (du Bray, 1996)			Unspecified deposits (see ref 1-4, 11,12 & 16 in Appendix 5.1)	
	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

Appendix 6.3: Predicted concentrations and distributions of major mineral groups and associated elements: Detailed mass balance calculations

Mass balance calculations for the derivation of compositions and distributions of major mineral groups and associated elements during concentration of copper sulphide ore deposits

1. $C_{m,conc}$(kg/t)

Mass balance equation	Assumptions
$C_{Fe,conc} = (0.304\ C_{chalcopyrite,\ conc} + 0.466\ C_{pyrite,\ conc} + 0.1113\ C_{bornite,\ conc})/0.85$ $C_{S,conc} = (0.349\ C_{chalcopyrite,\ conc} + 0.534\ C_{pyrite,\ conc} + 0.2552\ C_{bornite,\ conc} + 0.2011\ C_{chalcocite,\ conc})/0.96$ $C_{Cu,conc} = (0.347\ C_{chalcopyrite,\ conc} + 0.6334\ C_{bornite,\ conc} + 0.7988\ C_{chalcocite,\ conc})/0.99$ $C_{gangue,conc} = 1000 - (C_{chalcopyrite,\ conc} + C_{pyrite\ ,conc} + C_{bornite,\ conc} + C_{chalcocite,\ conc} + C_{minor\text{-}trace\ metal\ minerals,\ conc})$ $C_{silicate\ minerals,conc} = (0.9\ to\ 0.98)\ C_{gangue,conc}$ $C_{carbonate\ \&\ oxide\ minerals,\ conc} = C_{gangue,conc} - C_{silicate\ minerals,conc}$ $C_{quartz,conc} = 0.45C_{silicate\ minerals,\ conc}$ $C_{K\text{-}feldpar,conc} = 0.25C_{silicate\ minerals,\ conc}$ *m: biotite, muscovite and albite* $C_{m,conc} = 0.10C_{silicate\ minerals,\ conc}$ $C_{calcite,conc} = 0.70\ C_{carbonate\ minerals,\ conc}$ *m: dolomite, ankerite and siderite* $C_{m,conc} = 0.10C_{carbonate\ minerals,\ conc}$ $C_{si} = (0.47\ C_{quartz,conc} + 0.162\ C_{biotite,\ conc} + 0.197\ C_{feldspar,conc} + 0.222\ C_{albite,conc} + 0.211\ C_{muscovite,conc})/0.98$ $C_{Al} = (0.156\ C_{biotite,\ conc} + 0.190\ C_{feldspar,conc} + 0.214\ C_{albite,conc} + 0.204\ C_{muscovite,conc})/0.98$ $C_{K} = (0.075\ C_{biotite,\ conc} + 0.275\ C_{feldspar,conc} + 0.098C_{muscovite,conc})/0.98$ $C_{Na} = (0.183\ C_{albite,conc})/0.98$ $C_{Mg} = (0.07\ C_{biotite,\ conc} + 0.13\ C_{dolomite,conc})/0.98$ $C_{Ca} = (0.4\ C_{calcite,conc} + 0.217\ C_{dolomite,\ conc} + 0.345\ C_{ankerite,\ conc})/0.98$	• 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

Appendix 6.3: Predicted concentrations and distributions of major mineral groups and associated elements: Detailed mass balance calculations

Mass balance calculations for the derivation of compositions and distributions of major mineral groups and associated elements during concentration of copper sulphide ore deposits

1. $C_{m,conc}$(kg/t)

Mass balance equation	Assumptions
$C_{Fe,conc} = (0.304\ C_{chalcopyrite,\ conc} + 0.466\ C_{pyrite,\ conc} + 0.1113\ C_{bornite,\ conc})/0.85$ $C_{S,conc} = (0.349\ C_{chalcopyrite,\ conc} + 0.534\ C_{pyrite,\ conc} + 0.2552\ C_{bornite,\ conc} + 0.2011\ C_{chalcocite,\ conc})/0.96$ $C_{Cu,conc} = (0.347\ C_{chalcopyrite,\ conc} + 0.6334\ C_{bornite,\ conc} + 0.7988\ C_{chalcocite,\ conc})/0.99$ $C_{gangue,conc} = 1000 - (C_{chalcopyrite,\ conc} + C_{pyrite\ ,conc} + C_{bornite,\ conc} + C_{chalcocite,\ conc} + C_{minor\text{-}trace\ metal\ minerals,\ conc})$ $C_{silicate\ minerals,conc} = (0.9\ to\ 0.98)\ C_{gangue,conc}$ $C_{carbonate\ \&\ oxide\ minerals,\ conc} = C_{gangue,conc} - C_{silicate\ minerals,conc}$ $C_{quartz,conc} = 0.45C_{silicate\ minerals,\ conc}$ $C_{K\text{-}feldpar,conc} = 0.25C_{silicate\ minerals,\ conc}$ *m: biotite, muscovite and albite* $C_{m,conc} = 0.10C_{silicate\ minerals,\ conc}$ $C_{calcite,conc} = 0.70\ C_{carbonate\ minerals,\ conc}$ *m: dolomite, ankerite and siderite* $C_{m,conc} = 0.10C_{carbonate\ minerals,\ conc}$ $C_{Si} = (0.47\ C_{quartz,conc} + 0.162\ C_{biotite,\ conc} + 0.197\ C_{feldspar,conc} + 0.222\ C_{albite,conc} + 0.211\ C_{muscovite,conc})/0.98$ $C_{Al} = (0.156\ C_{biotite,\ conc} + 0.190\ C_{feldspar,conc} + 0.214\ C_{albite,conc} + 0.204\ C_{muscovite,conc})/0.98$ $C_{K} = (0.075\ C_{biotite,\ conc} + 0.275\ C_{feldspar,conc} + 0.098C_{muscovite,conc})/0.98$ $C_{Na} = (0.183\ C_{albite,conc})/0.98$ $C_{Mg} = (0.07\ C_{biotite,\ conc} + 0.13\ C_{dolomite,conc})/0.98$ $C_{Ca} = (0.4\ C_{calcite,conc} + 0.217\ C_{dolomite,\ conc} + 0.345\ C_{ankerite,\ conc})/0.98$	• 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* $(0.304\ C_{chalcopyrite,\ ore} + 0.466\ C_{pyrite,\ ore} + 0.1113\ C_{bornite,\ ore})/0.85$ *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.)= $M_{t\ ,tails}$ x 1.9 $C_{gangue,\ waste\ rock}$: Calculated (point 6)

6. $C_{m,\ waste\ rock}$

Mass balance equation	Assumptions
m = chalcopyrite, bornite, chalcocite, pyrite, minor/trace metal minerals, Fe and S, silicates, carbonates, Si, Al, Ca, Mg, K, Na $(D_{m,\ waste\ rock} \times C_{m,\ ore} \times M_{t,\ ore}) / M_{t,waste\ rock}$ *m = gangue* $1000 - (C_{chalcopyrite,\ waste\ rock} + C_{pyrite,\ waste\ rock} + C_{bornite,\ waste\ rock} + C_{chalcocite,\ waste\ rock} + C_{minor\text{-}trace\ metal\ minerals,\ waste\ rock})$	

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)

Appendix 6.4: Predicted distributions, concentrations and forms of individual elements in typical porphyry – type copper sulphide ores, concentrates and tailings

Mass balance calculations for the derivation of individual element enrichment factors and concentrations in copper sulphide ores, tailings and concentrates.

Mass balance equation	Assumptions
1. Empirical enrichment factors in ores for element m $(E_{m,\ tailings})_{empirical} = (C_{m,\ ore})_{empirical} / C_{m,\ crust}$	• 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.
2. Predicted element enrichment factors in tailings and concentrate for element m $E_{m,\ tailings} = (E_{m,\ ore} \times D_{m,\ tailings})$ $E_{m\ concentrate} = (E_{m,\ ore} \times D_{m,\ tailings})$	• 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 and 0.3 to 0.6% to the concentrate: i.e. $D_{gangue\ elements,\ tails}$ = 0.994 to 0.997 and $D_{gangue\ elements,\ conc}$ = 0.003 to 0.006
3. Predicted concentration ranges for element m Ore concentrations: $C_{m,\ ore} = (E_{m,\ ore} \times C_{m,\ crust})$ Tailings concentrations: $C_{m,\ tailings} = (D_{m,\ tails} \times C_{m,\ ore}) / (1-(1/M_{t,\ conc}))$ Concentrate concentrations: $C_{m,\ ore} = D_{m,ore} \times C_{m,\ ore} \times M_{t,ore}$	• Between 10 and 15% of the copper in the ROM ore reports to the tailings and 85 - 90% to the concentrate: i.e. $D_{Cu,\ tails}$ = 0.10 to 0.15 and $D_{Cu,\ conc}$ = 0.85 to 0.90 • Between 63% and 93% of the Fe and S in the ROM ore reports to the tailings and between 7 and 37% to the concentrate: i.e. $D_{Fe\ \&\ S,\ tails}$ = 0.63-0.93 and $D_{Fe\ \&\ S,\ conc}$ = 0.07 to 0.37 • Between 10 and 30% of trace to minor chalcophiles and siderophiles in the ROM ore report to the tailings and between 70 and 90% to the concentrate: i.e. $D_{m,\ tails}$ = 0.10-0.3 and $D_{m,\ conc}$ = 0.7 to 0.9 • 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)

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)

Predicted element speciation in copper sulphide ores, tailings and concentrates continued....

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	

Predicted element speciation in copper sulphide ores, tailings and concentrates continued....

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	

7

Screening and Prioritising Environmentally Significant Constituents in Copper Sulphide Tailings: Case Study 2

The copper-depleted sulphide tailings described in the previous chapter generally exit the flotation circuit in the form of slurry containing approximately 75% water with a pH of between 10 and 10.5. Thickening of the tailings prior to disposal on a tailings pond is common industry practice, with the thickener overflow generally being recycled back to the mill circuit. Conventionally, the thickener underflow, containing between 40% and 60% moisture, 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; Jarvis & Younger, 2000; Environment Australia, 1997; ICMM, 2002; 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.
- 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.

Accurate assessment of impacts is in turn needed in order to make informed and appropriate decisions regarding appropriate management strategies to minimise such impacts in the short-, medium- and long-term. The impacted land footprint, developed by Hansen (2004) and described briefly in Chapter 1 of this thesis, provides a straightforward yet rigorous approach to assess this impact. A typical copper sulphide tailings waste stream will, however, contain a multitude of constituents (see Table 6.6 in the previous chapter), and it is clearly neither practical nor desirable to develop separate impacted land footprint indicators for each of these. As discussed in a previous chapter (Section 2.3 of Chapter 2), it is possible to estimate and compare the relative environmental risks posed by the various constituents within a solid waste on the basis of their hazardous nature and potential availability for release to the environment under disposal conditions. In this way, strategic or environmentally significant constituents can be identified upfront, resulting in more informed and effective quantitative risk assessment studies (including empirical waste characterisation and/or predictive modelling).

This chapter of the thesis is concerned with the application of previously developed methodologies and criteria to identify key constituents of potential environmental significance within typical copper sulphide tailings waste streams under disposal conditions. To this end, data and information pertaining to the geochemical and hydrogeological properties of typical sulphide tailings impoundments, as available in the open literature, is first collected and assessed (Section 7.1). This knowledge, together with the chemical composition data generated in the previous chapter, forms the basis for the subsequent screening and ranking of constituents in accordance with their potential environmental significance (Section 7.2).

7.1 Overview of 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 dependent 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°C) 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 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; 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 dependent 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 dependent 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. 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 7.1. Detailed results are presented in Appendix 7.1.

Table 7.1: Reported compositions of pore waters within sulphide tailings impoundments (compiled from Al et al, 2000; Benner et al, 2000; Carlsson, 2002; Komitsas, 1998; Kontopoulos et al, 1995; Mwale, et al, 2005; Patinha et al, 2004, van Huyssteen, 1998)

	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

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). These pH buffered zones are indicated diagrammatically in Figure 7.1.

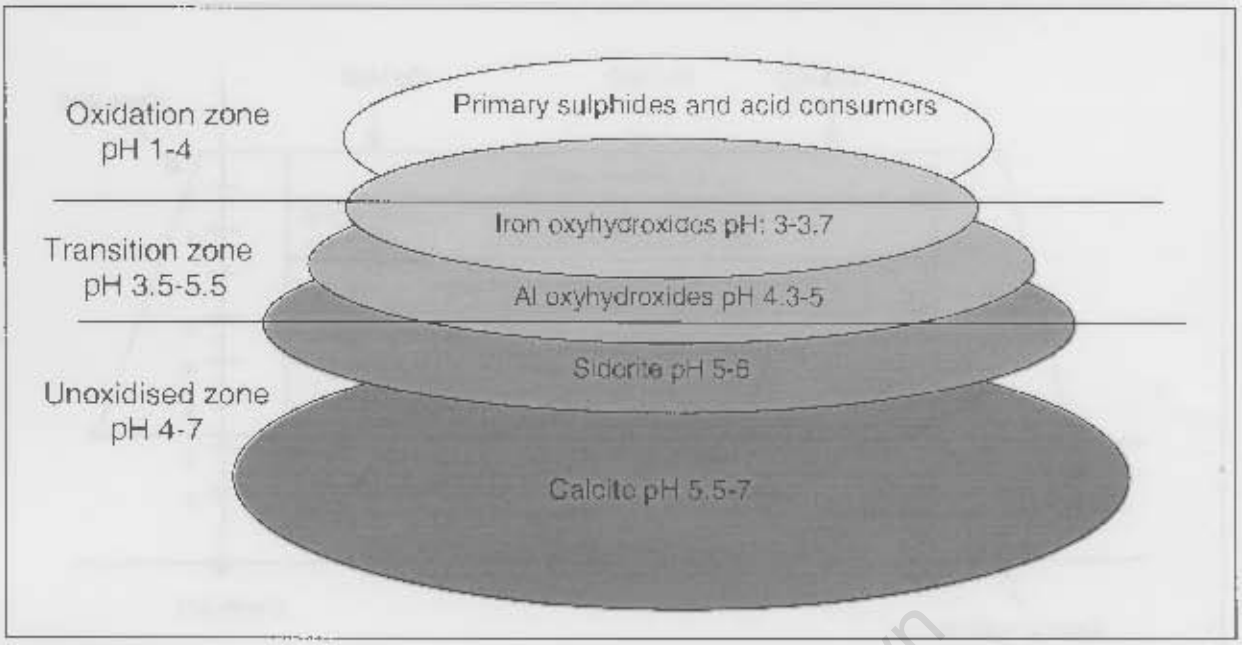


Figure 7.1: pH profiles and key controlling solid phases in tailings impoundments (based on the conceptual model of Morin et al, 1988)

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 7.1 and the trend plots in Appendix 7.1, 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. The typical spatially related contaminant concentration trends are illustrated graphically in Figure 7.2 overleaf.

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 dependent 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%.

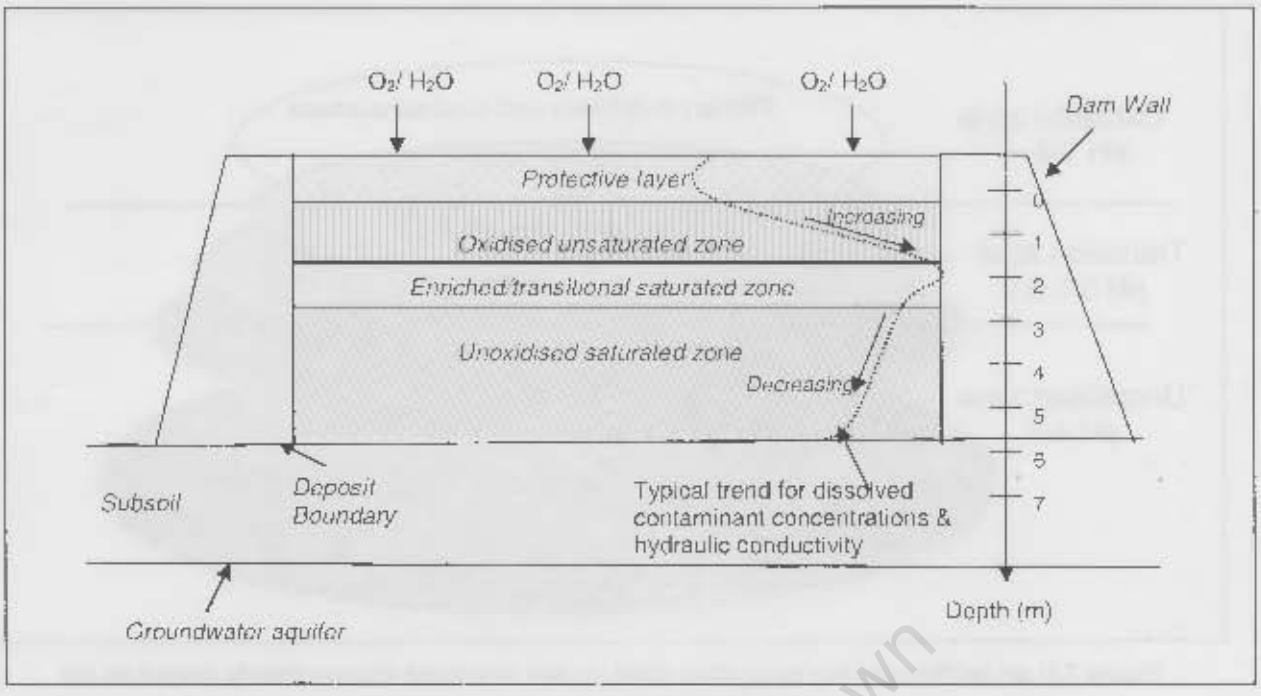


Figure 7.2: Conceptual spatial model of typical sulphide tailings impoundments

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 7.1) are presented in Table 7.2.

Table 7.2: 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 7.3. 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.

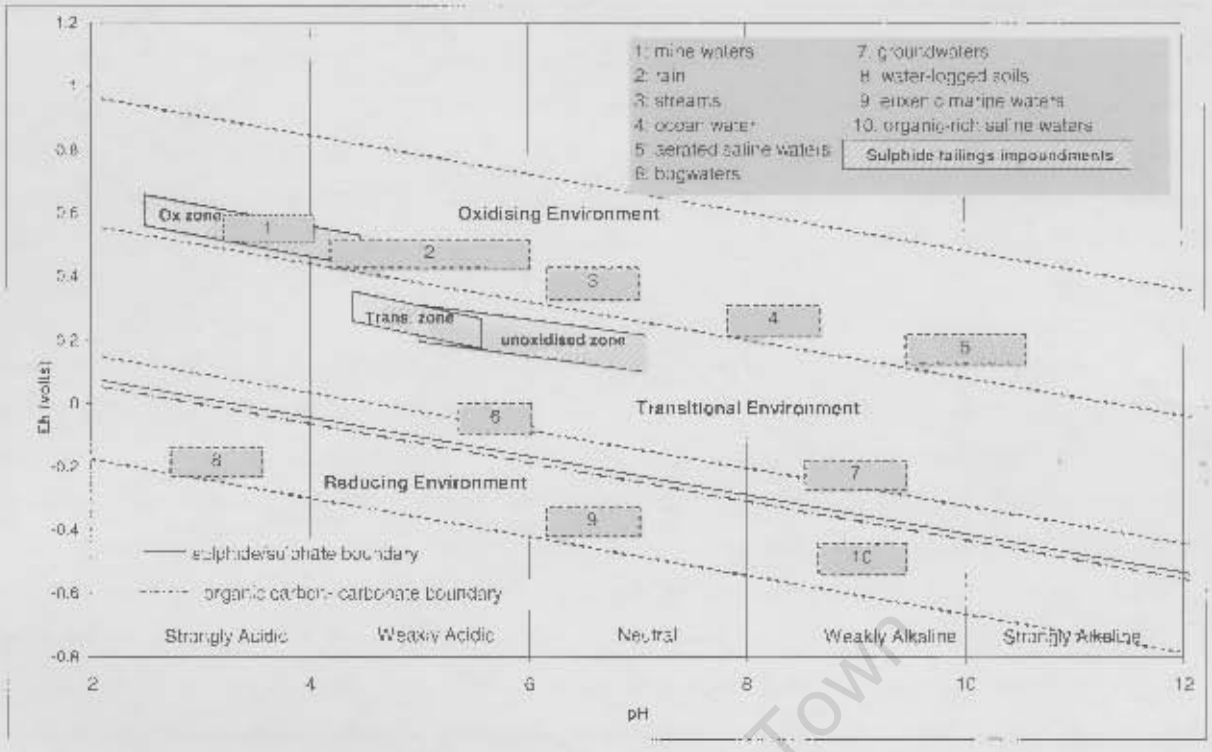


Figure 7.3: Generic Eh-pH diagram for tailings pore water and other water sources (modified from Garrels, 1960 and Brookins, 1988)

The properties of the pore waters arising from a specific tailings material will not only vary with depth (i.e. spatially), as illustrated in Figures 7.1 and 7.2, 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 dependent 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 behavior 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.

7.2 Screening and prioritising constituents in terms of potential environmental significance

As discussed in Chapter 2 of the thesis, the components of solid mineral wastes can be sub-divided into three main groups in terms of their potential impact on the surrounding environment, viz:

- **Major soluble salts:** This group includes the soluble salts, such as sulphates, carbonates, chlorides and phosphates, of the commonly occurring alkali metal (Na and K) and alkaline earth metal cations (Ca and Mg). 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, with elevated levels of TDS (total dissolved salts) being commonly linked to reduced plant productivity, as well as ecotoxicity and even human toxicity effects. In the case of porphyry-type copper sulphide tailings, the relatively high concentrations of dissolved sulphate (typically in the range of 5-25g/l) will contribute significantly (generally ≥ 70 %) to the TDS of the tailings pore waters.
- **Strategic trace-minor metals and metalloids.** This group includes metals and metalloids which generally only occur in soluble form in natural environments at relatively low concentrations, and which frequently exhibit ecotoxicity and mammalian toxicity effects if present at sufficiently elevated bioavailable levels. Many of the chalcophilic elements, such as Cd, As, Sb and Se, are both highly enriched in copper sulphide tailings relative to their average crustal abundance and highly toxic. Even iron and aluminium are generally relatively scarce in soluble form in natural environments,

and, although not highly toxic, can have a deleterious effect on the physical and aesthetic properties of water sources if present at elevated concentrations.

- **Acidity**: Acidity has a major influence on the environmental and biological availability of many metal and metalloids, and its impact is thus mostly indirect. Direct ecotoxicity effects, as well as impacts on the human consumption and the use of water sources will, however, also occur at low pH values (< 5.5).

This section of the thesis is concerned with the screening and ranking of constituents within typical copper sulphide tailings in accordance with the generic methodology developed within Chapter 2 of the thesis, as well as the information gained from the review in the previous section. As outlined in Figure 7.4, 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 (see Table 6.5 in Chapter 6), in a systematic and scientifically robust manner.

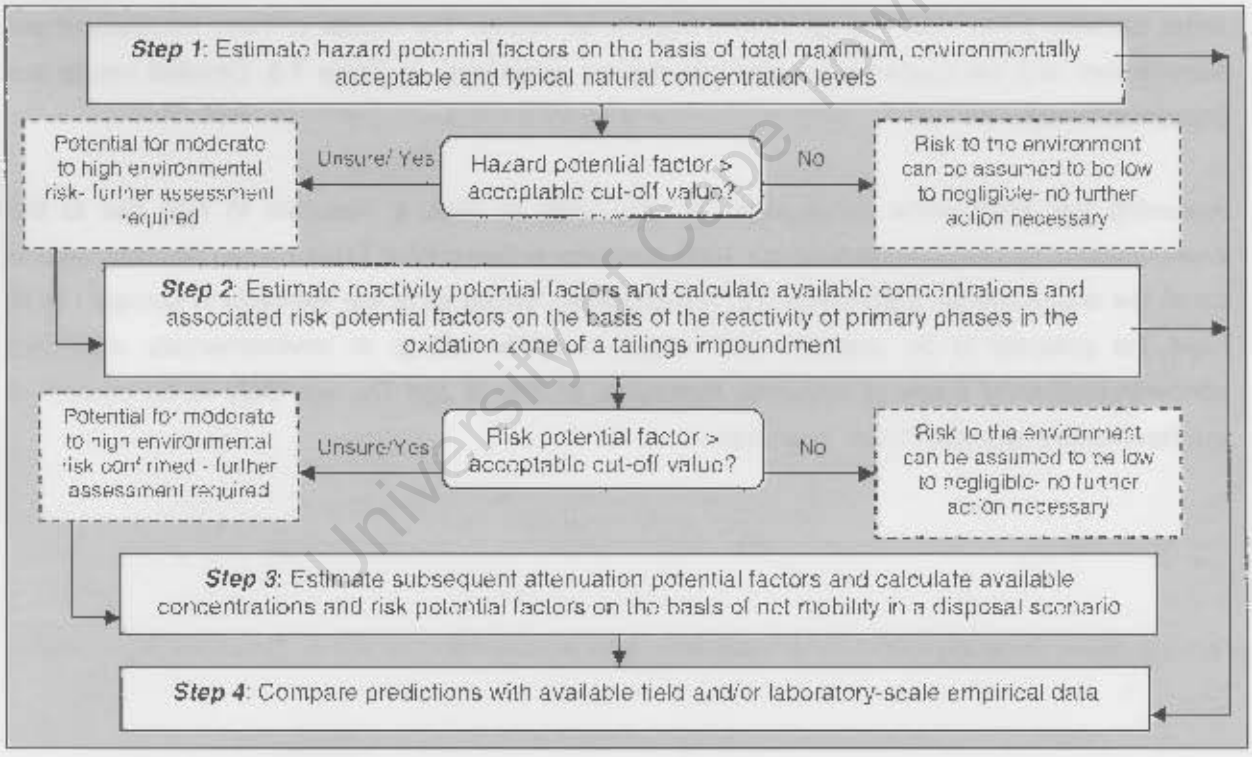


Figure 7.4: Procedural framework for the screening of potentially strategic constituents in copper sulphide tailings

7.2.1 Hazard potential predictions

In accordance with discussions in Chapter 2, 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, in accordance with Equation 2.3a-b.

Hazard potential factor = (*m.* effect factor).(*n.* enrichment factor)	Equation 2.3a
Hazard potential factor = (*m.n*)(solid concentration)^2 /((*m.*environmentally acceptable concentration).(*n.*typical natural concentration))	Equation 2.3b
Where *m* and *n* are weighting factors indicating the relative importance of the effect and enrichment factors	

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 (Section 2.3.2). 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 Chapter 6 of the thesis), 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 7.3. Detailed results are presented in Appendix 7.2.

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 7.3 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 S, Al, Fe, Si and Cu, are likely to be present at environmentally significant levels in *all* cases.

Table 7.3: 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 = $(m.n)(\text{solid concentration(ppm)})^2$ /[(m.water quality criteria (ppm)). (n.average crustal abundance (ppm))]

Assumptions:

- the effect and enrichement 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 hazard potential factors ≥ 1000
- elements in bold are likely to be of environmental significance even at the minimum predicted concentration levels (see Table 6.6 in Chapter 6 and detailed calculations in Appendix 7.2)

7.2.2 Reactivity, attenuation and availability potential factor predictions

As discussed in Chapter 2, 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 generic chemical behaviour model for solid mineral wastes deposits developed in Chapter 2 (see Figure 2.8), the fraction of a solid waste which is potentially available for release from a solid waste under disposal conditions can be predicted in three methodological steps. In the first step, that fraction of a solid constituent considered likely to be mobilised through weathering and alteration reactions of the primary phases is estimated and the associated risk potential factor calculated by substituting the reactive constituent concentration for total concentration in Equation 2.3b. The second step entails the estimation of the extent to which mobilised elements of potential environmental significance are likely to be attenuated through secondary precipitation and/or adsorption reactions.

Finally, 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 (typically 100 to 500 years (Hansen, 2004)), of elements is estimated in accordance with Equation 2.6.

Availability Potential Factor = Reactivity potential factor x (1-attenuation potential factor)	Equation 2.6
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	

Reactivity and associated risk potential factors for primary phase elements

In accordance with the review and assessment in Section 7.1, the weathering and alteration of primary phases within a sulphide tailings impoundment 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 slow, kinetically-controlled reaction mechanisms.

On the basis of general literature information (Ďuďa & Rejl, 1986; Thornton, 1983) and published pH-potential diagrams (Brookins, 1988; Garrels, 1960), the primary mineral phases typically occurring within porphyry-type copper sulphide flotation tailings (as identified in the previous chapter of the thesis) can be grouped in accordance with their thermodynamic stability under the likely Eh-pH conditions associated with the oxidation and transitional zones of a typical tailings impoundment, as described in Table 7.4.

Table 7.4: 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.		

Furthermore, as discussed in Chapter 5 (Section 5.2), the potential reactivity of the identified mineral phases can also be inferred from the results of empirical sequential chemical extraction (SCE) studies. Table 7.5 ranks the potential reactivity of elements in the primary zone of a base metal sulphide tailings impoundment based on the results of SCE tests conducted by Carlsson et al (2002) and Dold & Fontbote (2001).

Table 7.5: 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.				

Predictions pertaining to the potential reactivities of the primary phases and associated elements on the basis of the qualitative theoretical information (summarised in Table 7.4) and available empirical data (summarised in Table 7.5), are presented in Table 7.6.

Table 7.6: 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 in accordance with step 2 of the conceptual methodology outlined in Figure 7.4 (i.e. through the substitution of that fraction of each tailings constituent that is likely to be mobilised within the oxidation and transitional zones of the impoundment through primary dissolution reactions into Equation 2.3b), are presented in Table 7.7. Detailed results are presented in Appendix 7.2.

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.

Attenuation and availability potential factors for selected elements

As discussed in Section 7.1, 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.

Table 7.7: 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 B: 100-1000	A: Cd, Mo B: **Fe**, **S**, Ag, Se, Sb
III: Moderate environmental significance	A: 10-100 B: >1	A: Mn, Bi, **Al**, **Cu**, Pb B: Ni, Te, Hg, F, B, Zn, W
IV: Low environmental significance: non-strategic elements	A: 0.1-1 B: ≤ 0.1	A: REE, Si, Tl, Sn,Ca, Ti, Be,Mg, P, Ba 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 6.6 in Chapter 6 and detailed calculations in Appendix 7.2)

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 generated leachate. As discussed in Chapter 2 of the thesis, the chemical form or speciation is of particular relevance to the toxicity of metals and metalloids.

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 7.7), 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 has been provided in Chapter 5 of the thesis (see Box 5.1). The nature of the modelling output data is illustrated in Figure 7.5. Details in terms of model input data and derived Eh-pH diagrams are presented in Appendix 7.3.

	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-20
KSO4-	2.22E-10	1.86E-10
OH-	3.85E-12	3.17E-12
SO4-2	0.007283	0.003402

Fe(T): 10 00 ppm; S(T): 10 000 ppm

K(T): 1000 ppm; pH: 2.5; Eh: 650 mV

Solids	Concentration (M)
K-Jarosite	2.56E-2
Schwertmannite	4.36E-3

Component	% of total component concentration	Species name
Fe+2	70.706	Fe+2
	29.294	FeSO4 (aq)
K+1	97.699	K+1
	2.301	KSO4-
SO4-2	43.275	SO4-2
	20.956	FeSO4+
	1.933	Fe(SO4)2-
	7.512	HSO4-
	26.325	FeSO4 (aq)
Fe+3	4.464	Fe+3
	83.988	FeSO4+
	3.873	Fe(SO4)2-
	7.153	FeOH+2
	0.243	Fe(OH)2+
	0.274	Fe2(OH)2+4

Component	Total dissolved	% dissolved	Total precipitated	% precipitated
Fe+2	0.015124	100	0	0
Fe+3	0.004199	2.562	0.15974	97.438
H+1	0.004605	100	0	0
K+1	9.64E-09	0	0.025574	100
SO4-2	0.01683	16.167	0.08727	83.833

Figure 7.5: Example of the thermodynamic modelling output data: the K-Fe-S-H_2O system

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 7.8.

Table 7.8: 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

Table 7.8 continued.....

Element	Dominant attenuation mechanism(s)	Attenuation potential factor	Availability potential factor
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
Low attenuation			
Manganese	• Adsorption by ferrihydrite. • Partial precipitation of $MnCO_3$ possible at pH ≥ 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 7.6
- Pore water compositions, Eh-pH ranges and formation constants for precipitated phases as presented in Appendix 7.3
- 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.

7.2.3 Risk potential predictions

In accordance with the generic methodology outlined in Chapter 2, the available solid concentration levels and, ultimately, the risk potential factors for the various constituents can be derived from the predicted availability potential factors (Table 7.8), by means of Equations 2.5b and 2.4 respectively.

Available concentration = availability potential factor x total solid concentration	Equation 2.5b

Risk potential factor = $(m.n)$(available solid concentration)^2 /((m.environmentally acceptable concentration).(n.typical natural concentration))	Equation 2.4

The results of these calculations are summarised, and selected elements grouped and ranked accordingly, in Table 7.9. Detailed results are presented in Appendix 7.2.

Table 7.9: 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

Calculations: See Equations 2.5b and 2.4.

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 6.6 in Chapter 6 and detailed calculations in Appendix 7.2)

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

7.2.4 Reconciliation of predicted and available empirical data

Available data pertaining to the compositions of pore waters from actual sulphide tailings impoundments, as reported in the open literature, has been summarised in Table 7.1, and detailed in Appendix 7.1. This data is reconciled with typical drinking water quality guideline limits in Table 7.10 (A and B).

A comparison of the empirical data in Table 7.10 with the predictions reported in Table 7.9 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 result 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 7.10: 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 7.11 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 the 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 7.11: 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

7.3 Summary and concluding remarks

The aim of this chapter was to demonstrate the applicability of the generalised methodologies, scientific techniques and associated criteria, as developed in the previous chapters of the thesis, to screen and rank constituents within typical porphyry-type copper sulphide flotation tailings on the basis of their potential environmental significance under disposal conditions. This involved estimating and comparing the hazard and availability potentials of the various constituents at the generic concentration levels predicted within the previous chapter of the thesis, thereby highlighting the links in the ore formation→ ore extraction & beneficiation → waste disposal → environmental impact causal mechanism chain.

The outcomes of this case study have confirmed that it is necessary to consider three separate impacted land footprints in terms of the potential environmental impact posed by solid mineral wastes such as the copper sulphide tailings under disposal conditions, viz a salinity footprint, an acidity footprint and a metals footprint. Whilst consideration of total dissolved solids (TDS), or even dissolved sulphate concentrations, is appropriate for defining a salinity footprint and pH for defining an acidity footprint, development of an appropriate metals footprint requires the identification of a strategic metal, the footprint of which encompasses that of the other metals. Although the predictions in this chapter have identified a number of potentially strategic metals, including Mn, Fe, As, Zn, Cd, B, Mo, Se, Ni, Cu, Sb or even Si, their relative significance will be dependent on their actual waste-specific concentration levels. In line with discussions in the previous chapter this will, in turn, be largely dependent on the element concentrations within the feed ore and will vary according to the geological history and other physio-chemical properties of the site in which the deposit occurs.

Appendix 7.1: Available data pertaining to the chemical compositions of pore waters in generic sulphide tailings deposits

Reported pH, Eh and component concentration ranges as a function of impoundment zone

Parameter*	Surface zone			Oxidation zone							
	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 3 (Van Huyssteen, 1998)	Deposit 4 (Patinha et al, 2004)	Deposit 5 (Benner et al, 2000)	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	4.2	3.6	3.5	2.5	2.3	4
Redox (mV)	550	621	459		621	415	-	450	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	26802	-	3700	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	7886	2606	600	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	0.03	0.2	-	-	-	-
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	-	-	-	-	-

Reported pH, Eh and component concentration ranges as a function of impoundment zone continued.....

Parameter *	Transitional zone		Unoxidised zone					
	Deposit 2 (Al et al, 2000)	Deposit 3 (Van Huyssteen, 1998)	Deposit 1 (Carlsson, 2003)	Deposit 2 (Al et al, 2000)	Deposit 3 (Van Huyssteen, 1998)	Deposit 4 (Patinha et al, 2004)	Deposit 5 (Benner et al, 2000)	Deposit 6B (Kontopoulos et al, 1995)
pH	6.8	5.7	4.2	6.6	6.8	5.8	4.9	7
redox	217	359	-	165	354	-	350	330
TDS	13999	-	3459	7299	-	-	-	-
Ca	440	447	153	369	307	-	-	200
Mg	1780	1964	117	317	131			300
Na	720	70	8	160	97			
K	86	64	4	67	42			
sulphate	10080	21894	2229	5580	1440		3700	1000
Cl	54			16				
carbonate							5	
Cu	0.07	0.06	0.004		0.03			
Fe	254	6243	465	388	32		600	
Zn	421	1.3	361	388	<0.1			4
Pb	0.3	0.007	0.2	0.2	0.003			
As	0.05		0.1	0.02	<0.1	<0.02		
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

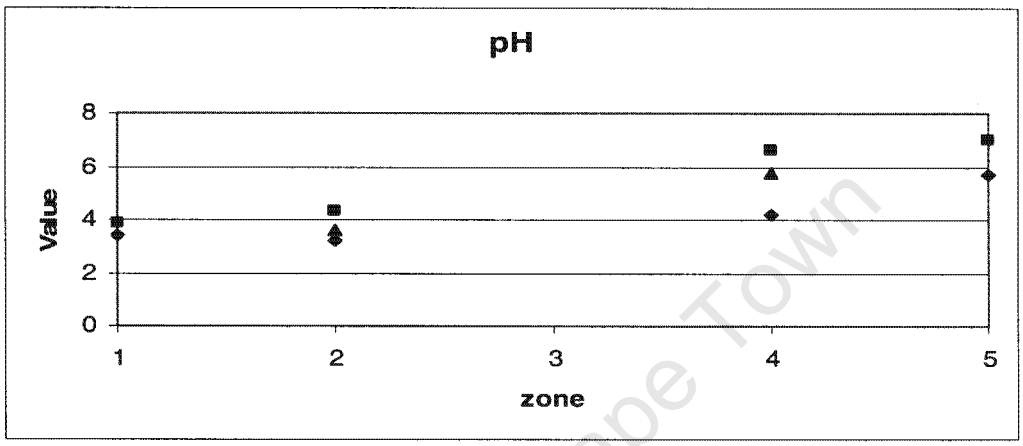
Reported pH, Eh and component concentration ranges as a function of impoundment zone continued.....

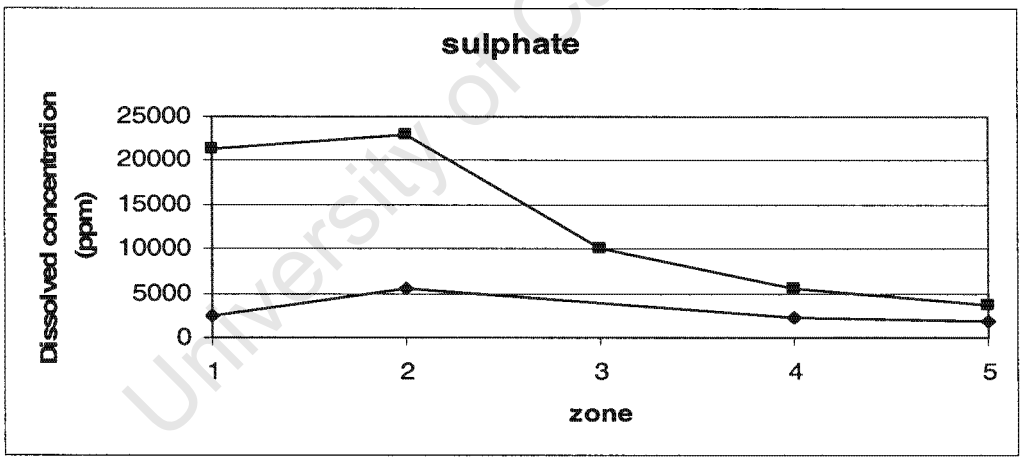
Parameter*	Groundwater interface zone					
	Deposit 1 (Carlsson, 2003)	Deposit 2 (Al et al, 2000)	Deposit 3 (Van Huyssteen, 1998)	Deposit 5 (Benner et al, 2000)	Deposit 7 (Mwale et al, 2005)	Deposit 8 (Komitsas, 1998
pH	5.7	7	7.8	6	7.1	5.8
redox		94	456	150		303
TDS	2903	4521				
Ca	444	451	97			106
Mg	45	175	26			24
Na	8	105	68			
K	3	22	16			
sulphate	1935	3740	48	3200	1989	
Cl		16.2			5	
carbonate				54		
Cu	0.002		0.02		0.3	
Fe	419	8	1	1300	0.3	
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			

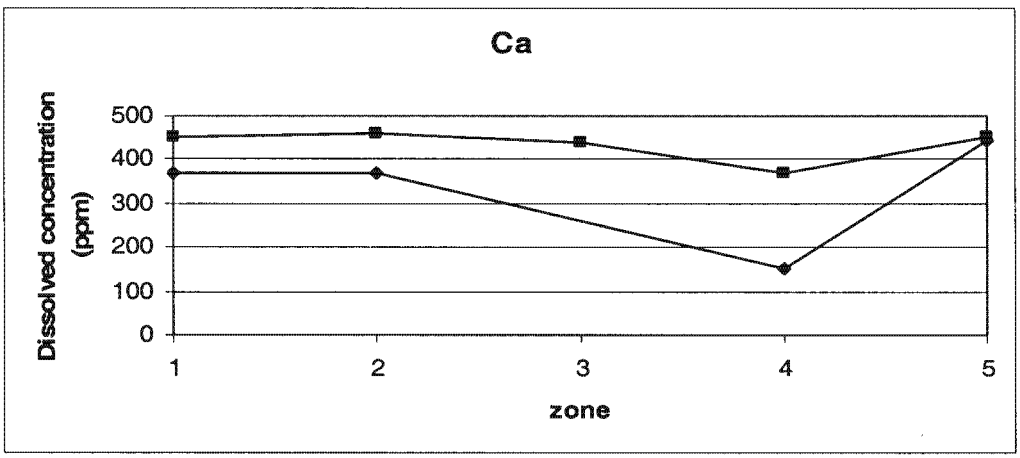
* All values except pH and redox potential in ppm

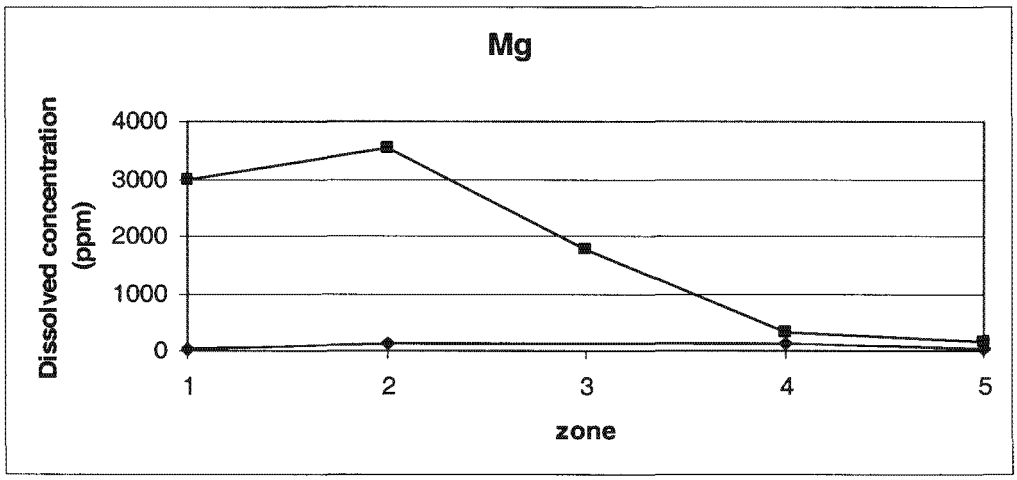
Tailings pore water concentration profiles as a function of depth

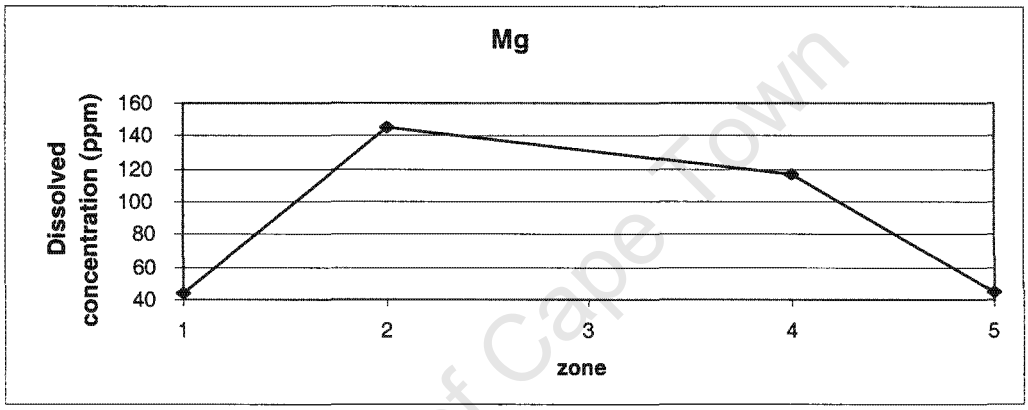
Zone 1: surface zone
Zone 2: oxidation zone
Zone 3: transition zone
Zone 4: unoxidised zone
Zone 5: groundwater interface zone

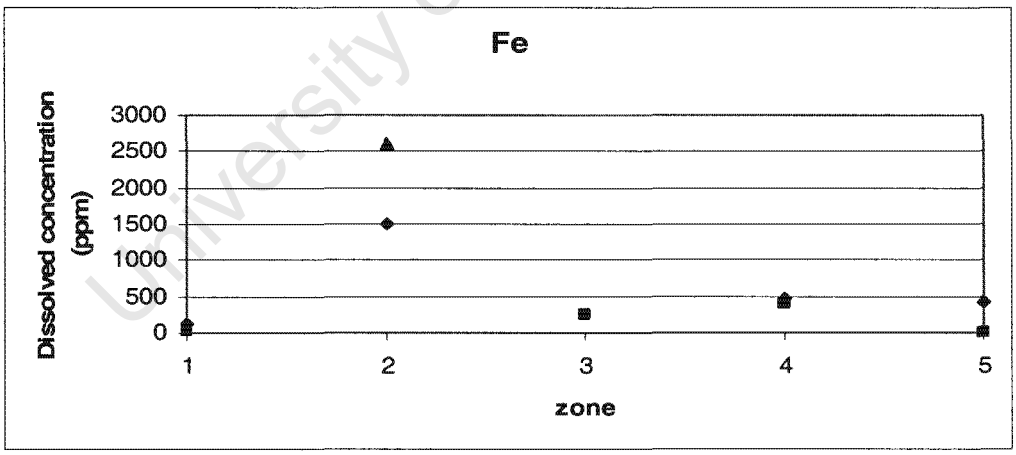


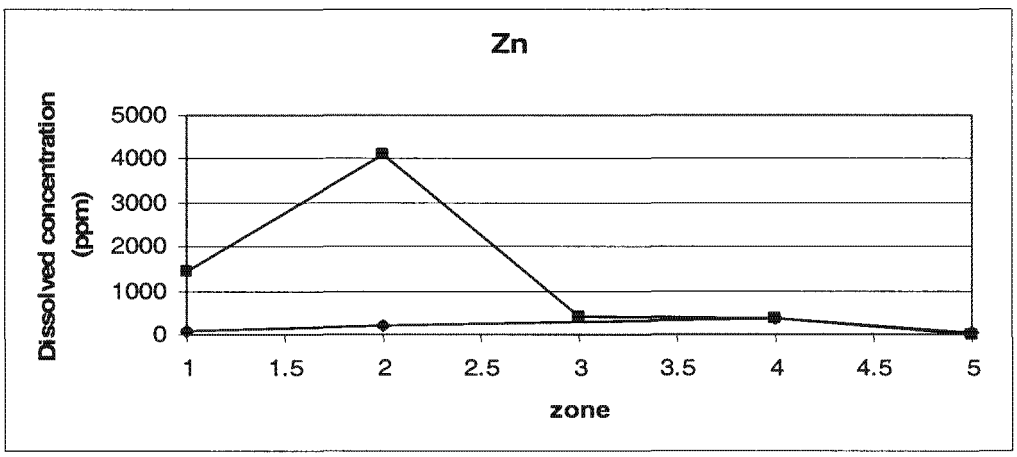


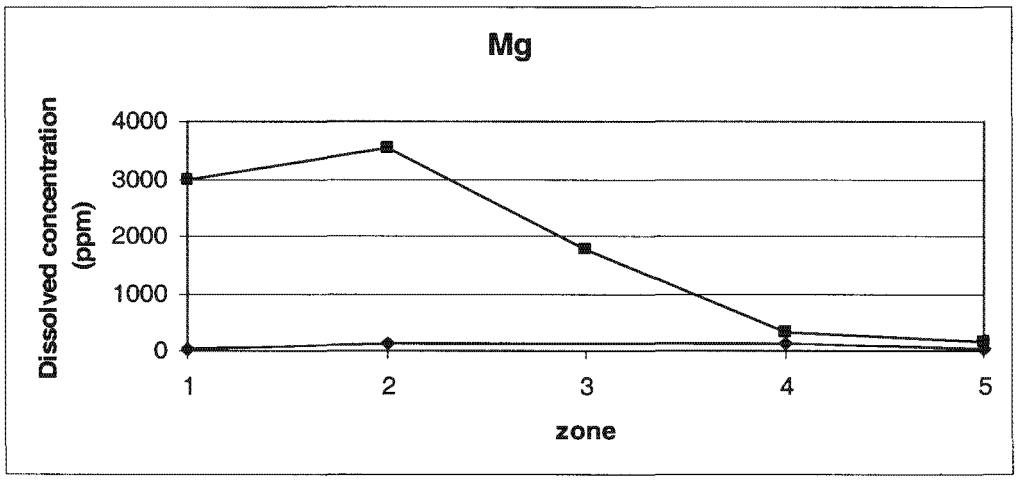


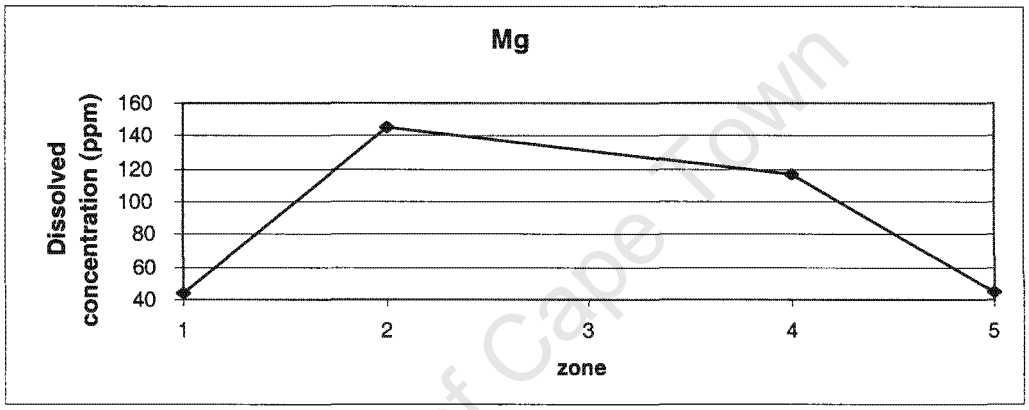


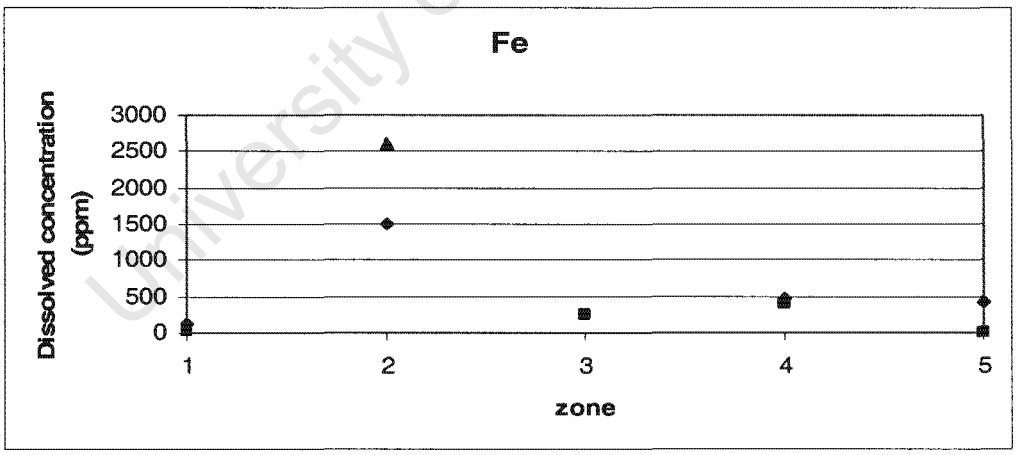


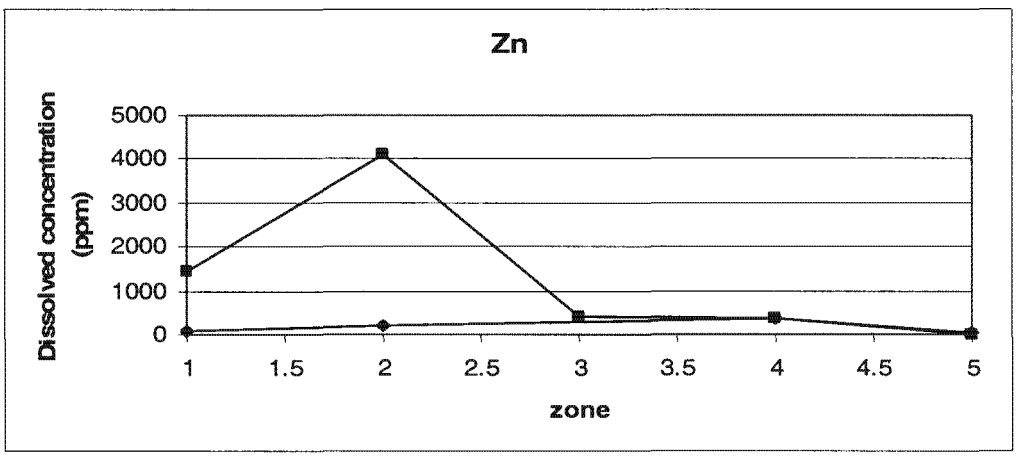


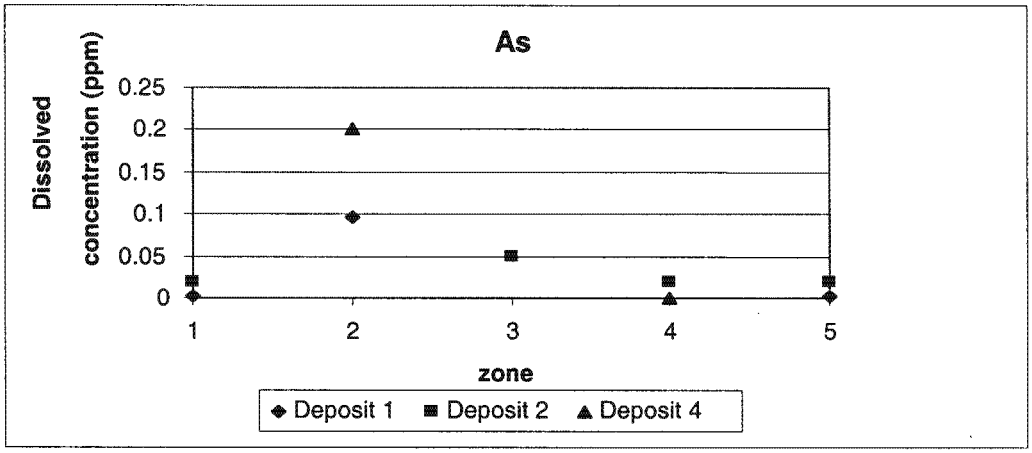












Description of Tailings:

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.

Appendix 7.2: Derivation of generic hazard and risk potential factors for porphyry-type copper sulphide tailings

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	8000-95000	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	800-1300	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
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

Hazard potential factors continued....

Component	Predicted concentration range (ppm)	Crustal abundance (ppm)	Typical guidelines for drinking water (ppm)	Hazard potential factors/1000	
				Minimum	Maximum
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

Predicted concentration ranges refer to predictions conducted within Chapter 6 of the thesis (Table 6.6)

Crustal abundance values are sourced from Cotton & Wilkinson (1962) and Cox (1995)-see Appendix 2.2, Chapter 2.

Drinking water values are sourced from ANZECC (1999) and DWAF (1996)-see Appendix 2.1, Chapter 2.

*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.

Hazard potential factor = (element concentration in solid (ppm))^2 / (crustal abundance (ppm)x typical water quality guideline limits (ppm))

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	<0.01-0.03	<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 / (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

Appendix 7.3: Thermodynamic modelling of attenuation reaction mechanisms: Model input parameters

Eh-pH of pore waters

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 ranges

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

Equilibrium formation constants for secondary solid phases

Element	Species	Log K_f	Source	ΔG_f (kJ/mol)	Source
Ca	Gypsum ($CaSO_4.2H_2O$)	4.61	MINTEQA2 ver.4 database	-1797.39	Calculated from Log K_f (4.61)
				-1797.12	HSC ver. 5.1 database
	Calcite ($CaCO_3$)	8.48	MINTEQA2 ver.4 database	-1129.1	Calculated from Log K_f (4.61)
Fe	K-jarosite ($KFe_3(OH)_6(SO_4)_2$	11.0	MINTEQA2 ver.4 database; Baron & Palmer (1996)	-3309.71	Calculated from Log K_f (11.0)
		9.21	PHREEQC database	-3017	Calculated from Log K_f (9.21)
	Schwertmannite ($Fe_8O_8(OH)_6(SO_4)$)	-18	Bigham et al (1996)	-4104.21	Calculated from Log K_f (-18)
	Ferrihydrite ($Fe(OH)_3$)	-2.69	MINTEQA2 ver.4 database (aged ferrihydrite)	-713.94	Calculated from Log K_f (-2.69)
				-798.98	HSC ver. 5.1 database
	Siderite ($FeCO_3$)	10.59	MINTEQA2 ver.4 database	-679.86	Calculated from Log K_f (10.59)
				-666.67	HSC ver. 5.1 database
Al	Alunite ($KAl_3(OH)_6(SO_4)_2$)	1.4	MINTEQA2 ver.4 database	-4663.76	Calculated from Log K_f (1.4)
	Jurbanite ($AlOHSO_4$)	3.23	MINTEQA2 ver.4 database	-1487.05	Calculated from Log K_f (3.23)
	Gibbsite ($AlOOH$)	-7.74	MINTEQA2 ver.4 database	-1154.73	Calculated from Log K_f (-7.74)

Equilibrium formation constants for secondary solid phases continued...

Element	Species	Log K_f	Source	ΔG_f (kJ/mol)	Source
Si	Kaolinite $Al_2Si_2O_5(OH)_4$	-7.44	MINTEQA2 ver.4 database	-3834.63	Calculated from Log K_f (-7.44)
	Amorphous SiO_2	2.74	MINTEQA2 ver.4 database	-873.83	Calculated from Log K_f (2.74)
Mn	Rhodochrosite ($MnCO_3$)	11	MINTEQA2 ver.4 database	-818.671	Calculated from Log K_f (11.0)
				-816.62	HSC ver. 5.1 database
	Hausmannite (Mn_3O_4)	-61.03	MINTEQA2 ver.4 database	-1284.33	Calculated from Log K_f (61.03)
				-1283	HSC ver. 5.1 database
	Manganite	-25.34	MINTEQA2 ver.4 database	-557.693	Calculated from Log K_f (-25.34)
				-567.13	HSC ver. 5.1 database
	Pyrolusite	-41.38	MINTEQA2 ver.4 database	-466.171	Calculated from Log K_f (-41.38)
				-465.0	HSC ver. 5.1 database
Cu	Covellite (CuS)	22.27	MINTEQA2 ver.4 database	-49.4351	Calculated from Log K_f (22.27)
	Chalcocite (Cu_2S)	34.65	MINTEQA2 ver.4 database	-85.66	Calculated from Log K_f (43.65)
				-86.22	HSC ver. 5.1 database
				-1307.5	??

Equilibrium formation constants for secondary solid phases continued....

Element	Species	Log K_f	Source	ΔG_f (kJ/mol)	Source
Mo	$CaMoO_4$	7.95	MINTEQA2 ver.4 database	-1434.36	Calculated from Log K_f (7.95)
				-1435.54	HSC ver. 5.1 database
Pb	Anglesite ($PbSO_4$)	7.79	MINTEQA2 ver.4 database	-812.41	Calculated from Log K_f (7.79)
				-812.407	HSC ver. 5.1 database
	Cerrusite ($PbCO_3$)	13.2	MINTEQA2 ver.4 database	-603.225	Calculated from Log K_f (13.2)
				-625.378	HSC ver. 5.1 database
Sb	$Sb(OH)_3$	7.11	MINTEQA2 ver.4 database	-685.188	Calculated from Log K_f (7.11)
	Sb_2O_4	-3.40	MINTEQA2 ver.4 database	-795.548	Calculated from Log K_f (-3.40)
				-795.89	HSC ver. 5.1 database
	Sb_4O_6	17.90	MINTEQA2 ver.4 database	-1257.78	Calculated from Log K_f 17.90)
				-1249.4	HSC ver. 5.1 database
Se	Cu_2Se	45.8	MINTEQA2 ver.4 database	-117.549	Calculated from Log K_f (45.8)
				-73.233	HSC ver. 5.1 database
Bi	Bi_2O_3	-4.066	Calculated from Gibbs free energy of formation	-118.809	HSC ver. 5.1 database; Garrels (1960); Kneen et al (1972)
Zn	$ZnCO_3$	10.8	MINTEQA2 ver.4 database	-736.781	Calculated from Log K_f (10.8)
				-731.476	HSC database
				-1307.5	??

Equilibrium formation constants for secondary solid phases continued....

Element	Species	Log K_f	Source	ΔG_f (kJ/mol)	Source
				-731.476	HSC database
Ba	Barite ($BaSO_4$)	9.98	MINTEQA2 ver.4 database	-1362.15	Calculated from Log K_f
				-1347.86	HSC ver. 5.1 database
	Witherite ($BaCO_3$)	8.57	MINTEQA2 ver.4 database	-1137.65	Calculated from Log K_f
				-1135.32	HSC ver. 5.1 database
Cd	Otavite ($CdCO_3$)	12.01	MINTEQA2 ver.4 database	-674.144	Calculated from Log K_f
				-670.53	HSC ver. 5.1 database
As	Scorodite ($FeAsO_4.2H_2O$)	20.2 (scenario 1)	MINTEQA2 ver.4 database	-1255.8	Calculated from Log K_f
				-1307.5	??

8

Predicting Element Distribution during Matte Smelting of Copper Sulphide Concentrates: Case Study 3

As indicated in Chapter 6, the pyrometallurgical processing of copper sulphide concentrates comprises two primary unit operations (smelting and converting), as well as a number of possible secondary operations, including slag cleaning, treatment of furnace flue dusts, and sulphuric acid production. This chapter of the thesis demonstrates the application of the proposed generic approach and associated criteria for predicting element distribution during smelting of copper sulphide concentrates. In this regard, the available and relevant data and information pertaining to the smelting process are first collected and assessed (Section 8.1). This is followed by a fundamental assessment of the key chemical properties and potential distribution behaviours and associations of elements during the smelting process, on the basis of theoretical chemical and thermodynamic principles (Section 8.2). Finally, the knowledge gained through such a study is used to rationalise available empirical distribution data and address data gaps, ultimately resulting in a comprehensive list of element distribution factors during smelting, as a function of key reactor variables (Section 8.3).

8.1 Background information and available data

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 section of the thesis is specifically concerned with data and information pertaining to the concentrations and distributions of typical copper sulphide ore components during the matte smelting operations.

Smelting with a siliceous flux to produce a sulphide matte rich in copper forms the first step in the pyrometallurgical processing of copper sulphide concentrates. Traditionally smelting was carried out in reverbatory furnaces, either with or without a pre-roasting step, and as late as 1975 accounted for most of the world's copper smelting. Recent decades have seen the development of a number of new smelting processes, which have significant advantages over reverbatory and electric furnace smelters, particularly with regards to energy efficiency and the avoidance of atmospheric SO_2 emissions. In particular, flash smelting (Outokumpu and Inco processes) has become the most widely adopted smelting process since 1970 and accounts for most of the copper smelting in Japan and the United States. Other emerging smelter technologies receiving increasing recognition include the Noranda, Teniente, Mitsubishi, Isasmelt and the Contop processes. All of the modern smelting processes use the heat from Fe and S oxidation for heating and melting, rather than relying exclusively on external forms of energy, and produce off-gases with relatively high concentrations of SO_2, thus simplifying their capture and conversion to valuable by-products (mainly sulphuric acid). As a result of increasingly stringent environmental legislation and improvements in smelter technologies, the capture and recovery of SO_2 from off-gases has become a standard unit operation in all modern copper smelter plants.

Matte smelting of copper sulphide concentrates is generally conducted at temperatures of between 1100 and 1300°C in the presence of oxygen enriched air and a silica flux, and produces three primary output streams, viz:

- ***copper-rich matte***

  The matte is comprised mainly of copper, iron and sulphur with the general stoichiometry $Cu_2S.FeS$, and copper grades of between 40% and 75%. Higher grade copper mattes, as generally produced in flash smelting or continuous smelting operations, are generally more extensively oxidised and have a much lower FeS content than the lower grade copper mattes, such as those produced during reverbatory smelting. Most modern smelters produce a matte phase containing between 55% and 75% copper.

- ***iron silicate slag***

  Smelter slags are comprised mainly of silicates of iron (fayalite, $2FeO.SiO_2$) and, to a lesser extent, aluminium and alkaline earth metals. Oxides of copper and iron (magnetite) are frequently also present as significant components.

- ***SO_2 - rich gas***

  Apart from SO_2, the smelter off-gases generally contain significant quantities of fine grained solid material, blown through and out of the furnace before it can settle in the matte and slag phases, as well as ore components which are volatile under the smelting conditions. The solids are normally recovered in electrostatic precipitators, with simultaneous condensation of the majority of the volatile ore components, prior to recovery of SO_2, normally in the form of a sulphuric acid by-product.

A survey of available data pertaining to the compositions of the smelter output streams (see Appendix 6.1 of Chapter 6), indicates that, as in the case of the early beneficiation stage streams, currently available data, particularly pertaining to the less commonly occurring co-elements, are insufficient and generally of poor quality.

Similarly, whilst the distribution behaviour of the targeted metal and major ore components is generally fairly well understood, available data pertaining to distribution of minor to trace co-elements during the matte smelting process, as summarised in Table 8.1, are limited mainly to commonly occurring impurities. Furthermore, whilst it is clear that the matte grade (or extent of oxidation during smelting) has a significant effect on the distribution of elements, the extent and nature of the effect appears to vary in a somewhat erratic manner.

Table 8.1: Element distributions during smelting of copper sulphide concentrates: Available data (compiled from Biswas & Davenport, 1994; Hoh et al, 1983; Riveros & Utgard, 2003)

Element	Vapour phase		Slag phase		Matte phase	
	55% Cu matte	75% Cu matte	55% Cu matte	75% Cu matte	55% Cu matte	75% Cu matte
Arsenic	76-85	42	10-17	32	10	26-28
Lead	70	42	10	27	20	31
Bismuth	80	46	5	37	15	17
Zinc	40	23	45	66	15	11
Nickel	5	3	45	27	50	70
Selenium	20	19	5	46	75	35
Antimony	40	56	30	17	30	27
Cadmium	-	64	-	19	-	17
Mercury	-	89	-	1	-	10
Precious metals	-	-	-	-	99	-
Al, alkali metals, alkaline earth metals	-	-	majority	majority	-	-

8.2 Fundamental assessment of element distribution during smelting

Discussions in Chapter 4 (Section 4.3.2) of the thesis have indicated that the distribution behaviour of elements during smelting operations will be dictated mainly by their modes of occurrence in the feed concentrate and the chemical properties and reactions of such forms under smelting conditions. In the case of sulphide matte smelting operations, distribution of elements between the matte and slag phases will be dictated largely by the relative stabilities of their sulphide and oxide compounds under smelting conditions. Elements reporting preferentially to the matte phase will include those elements forming stable and non-volatile covalently bonded compounds with "soft" sulphide-type ligands (including tellurides, selenides, and arsenides) and/or uncombined metals under smelting conditions. Those elements forming non-volatile ionic compounds with "hard" oxide type ligands (including complex oxides such as silicates and carbonates) can be expected to report preferentially to the slag phase. Elements forming volatile compounds will mainly occur in the vapour phase.

The dominant reaction and distribution pathways during smelting are illustrated diagrammatically in Figure 8.1.

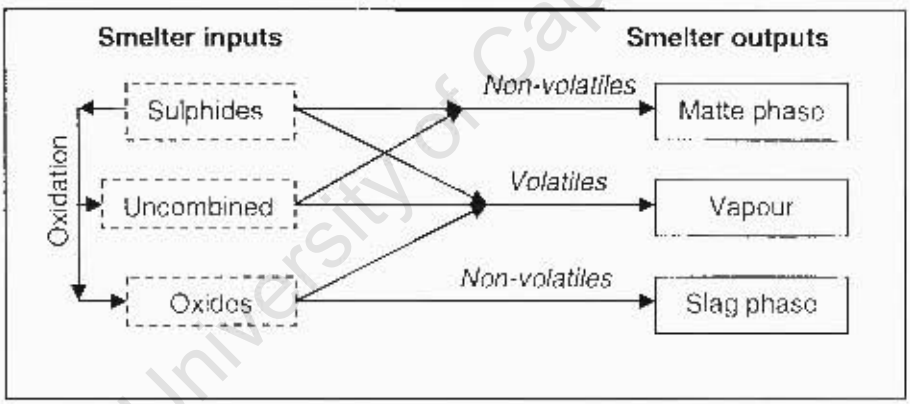


Figure 8.1: Element reaction and distribution pathways during copper matte smelting

The distribution behaviour of elements during matte smelting will thus be dictated mainly by:

- the chemical forms of the elements in the feed concentrate
- the rate and extent to which sulphide compounds are converted to oxides or metals under smelting conditions
- the rate and extent of volatilisation of stable forms (sulphides, oxides, uncombined) of the elements at typical smelting temperatures
- The extent of feed material blow-out into the gas stream

The effects of these factors on the properties and distribution behaviours of elements are discussed in detail in Sections 8.2.1 to 8.2.3. A detailed example to illustrate how a qualitative understanding of the deportment of Zn and Cd during matte smelting of copper sulphide concentrates can be achieved

through consideration of the fundamental chemical properties of the elements is provided in Chapter 5 (Box 5.2).

8.2.1 Chemical compositions of the feed concentrate

In accordance with the predictions in Chapter 6 of the thesis, the elements potentially occurring within a typical copper sulphide concentrate can be grouped into three main classes in terms of their forms, as indicated in Table 8.2.

Table 8.2: Classification of elements potentially occurring in copper sulphide concentrates

Group description	Elements	Potential deportment during smelting
Chalcophilic elements occurring predominantly as sulphide ore minerals	A: Cu, Fe, S B: Zn, Pb, Mo, As, Sb, Bi, Cd, Ni, Se, Ge, Ag, Co C: Tl, Hg, Tl, In, Re	Matte, slag and/or vapour depending on the stable forms under smelting conditions and volatility of such.
Siderophilic elements occurring as trace ore components, in either an uncombined/ native form or as " sulphide-type" compounds	C: Au, PGMs	As above
Lithophilic elements occurring predominantly as oxides (including silicates and carbonate) gangue minerals	B: Si, Al, K, Ca, Na, K, Mg, Ti, P C: F, Mn, B, Cl, Ba, REE, Rb, Sr, Zr, V, Li, Sn, Cr, Nb, Ga, W, Sc D: Ta, Be, Br, Hf, I, U	Slag or vapour, depending on the volatility of oxides at smelting temperature
The relative abundance of each major group of elements can be expected to decrease in the order A>B>C>D.		

8.2.2 Stable forms and miscibility of elements under smelting conditions

Covalently bonded sulphide compounds are generally less stable than ionic oxide compounds, particular at elevated temperatures. Hence, in the presence of oxygen, sulphides are unstable and will be converted to oxides, as indicated by the standard Gibbs free energies for the oxidation reaction in Equation 8.1

$2MS + 3O_2 \leftrightarrow 2MO+2SO_2$ $\Delta G^{\circ}(reaction)=\Delta G_f^{\circ}(oxides)- \Delta G_f^{\circ}(sulphides)$	Equation 8.1

In complex systems, however, the driving force for the oxidation of any particular minor or trace sulphide compound will depend on the Gibbs free energy of oxidation for that sulphide compound relative to that for the major sulphide compounds, viz copper and iron. A plot of standard Gibbs free energies of oxidation for the sulphide compounds of the chalcophilic and siderophilic elements, as presented in Figure 8.2, provides a measure of the relative stabilities of the oxide and sulphide forms of these elements.

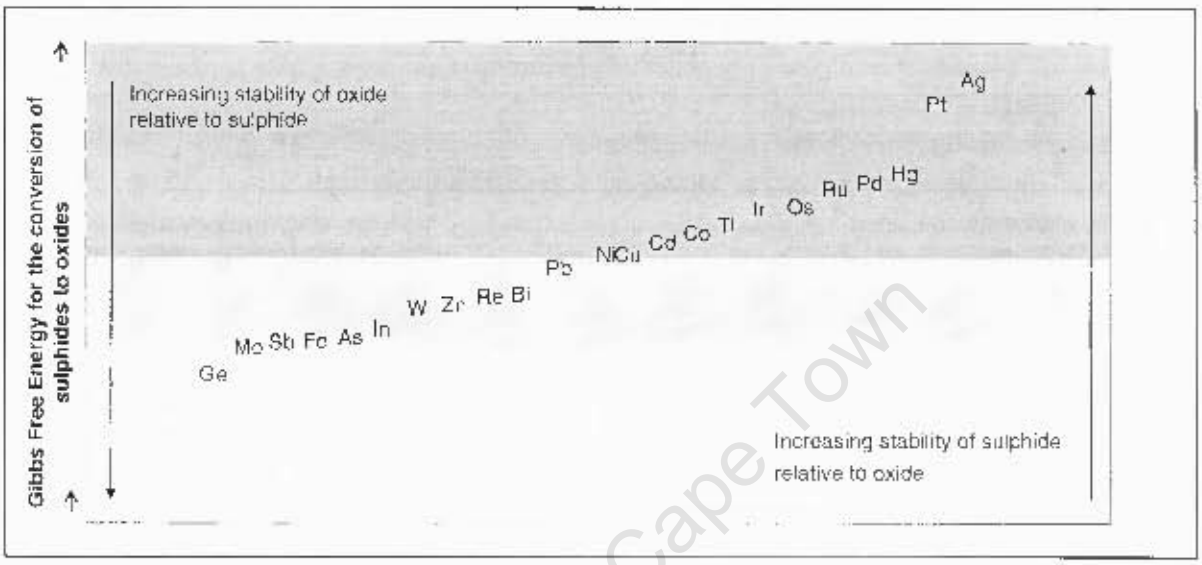


Figure 8.2: Relative stabilities of oxides and sulphide forms of the chalcophilic and siderophilic elements (Thermodynamic data sourced from Brookins, 1988; Cotton & Wilkinson, 1962; Elliot & Gleiser, 1960-63; Garrels, 1960; Knacke et al, 1991; Kneen et al, 1972; Lide, 1997; Price, 1998; Woods & Garrels, 1987; Zeimack, 1992)

As indicated in Table 8.3, chalcophilic elements in the sulphide ore concentrate can thus be grouped according to the relative chemical stabilities and behaviours of their sulphide and oxide forms during smelting, on the basis of equilibrium thermodynamics under standard steady conditions. The sulphide compounds of a number of the chalcophilic elements have stabilities which are intermediate between those of iron and copper. The extent and/or rate of oxidation of these sulphides is thus predicted to be highly dependent on the Cu/Fe ratio in the matte i.e. on the extent of oxidation of the major elements. Under "weakly "oxidising smelting conditions (process conditions which produce mattes with relatively low copper grades or high Fe/Cu ratios) these elements will probably occur in the sulphide form to a significant extent. The opposite trend can be expected under strongly oxidising smelting conditions (those producing high copper mattes as occur in Noranda and Teniente smelting furnaces), with significant oxidation of sulphides likely to occur.

Table 8.3: Relative stabilities of chalcophilic compounds and chemical behaviours under smelting conditions

Group description	Elements	Predicted stable forms under smelting conditions
Elements whose sulphide or metallic compounds are more stable than both the major sulphide elements (iron and copper)	Ag, Hg, Tl, Cd, Co, Ni, Cu	Such elements are likely to remain in the sulphide or metallic state during smelting.
Elements for which the relative sulphide compound stabilities are intermediate between those of iron and copper.	Pb, Zn, Bi, Re, In, As, Sb, Fe	The extent, to which these elements will occur in the sulphide or oxide form under smelting conditions, is likely to be highly dependent on the degree of oxidation or copper-matte grade.
Elements whose sulphide or metallic compounds are less stable to oxidation than both the major sulphide elements (iron and copper)	Mo, Ge	Such elements are likely to occur mainly in the oxide form under smelting conditions.

Whilst consideration of standard Gibbs free energies of oxidation provides an indication of the most stable forms and/or *major* reaction pathways under smelting conditions, in practice disequilibrium effects result in individual elements being present in more than one oxidation state and/or form, and distributed across more than one process stream at any given moment. As in the case of the element behaviour during formation of magmatic mineral deposits, a better understanding of these disequilibrium effects and multi-pathway distributions during high temperature processing can be gained by considering other properties, such as ionic radii and the nature and type of bonds formed, which influence the distribution behavioral patterns of elements at high temperatures.

The effect of ionic radii and charge density in ionic oxide compounds, on the relative properties and behaviours of the elements under thermal melting conditions has been discussed in detail in Chapter 3. On the basis of these properties ionic substitution (Figure 3.9) and oxide miscibility (Figure 3.7) models have been constructed indicating feasible associations of oxide forms of trace and minor elements with the ionic compounds of major mineral-forming elements. In contrast to oxide compounds, the chemical properties of the covalent sulphide compounds at elevated temperatures are determined largely by the extent of metal-metal bonding or alloy- like character of the compounds. Copper sulphide mattes are extremely good conductors, indicating a high degree of metal-metal bonding or alloy-like character. Hence it can be assumed that the miscibility of covalently bonded metal compounds with the matte will increase as the extent of metal-metal bonding in their compound structures increases. Kneen et al (1972) report that metal selenides and tellurides are even more alloy-like in character than the sulphides, and to a lesser extent so are metal antimonides and arsenides. Although metal sulphides

frequently have peculiar and complex stoichiometries, and are generally not well understood. sulphides reported by Cotton and Wilkinson(1962) to have extensive metal-metal bonding include those of Ni, Fe and Co. Other alloy-like sulphides are those of Pb and, to a lesser extent, Zn and Cd.

Predictions pertaining to the miscibilities or associations of trace to minor chalcophilic elements with major matte and slag forming minerals on the basis of ionic radii, charge densities (oxide compounds) and metal-metal bonding (sulphide compounds), are presented in Table 8.4

Table 8.4: Predicted trace to minor element associations with major matte and slag forming elements

Major matte and slag forming elements	Predicted trace to minor elements associations	
	On the basis of ionic radii	On the basis of the nature and structure of the sulphide and oxide compounds
Matte-Phase		
S(-II)	Se(-II)	Se(-II), Te(-II) > Sb(-III)>As(-III)
Cu(I)	Cd(II), Tl(III)	Ni(II), Co(II)> Pb(II)> Zn(II), Cd(II)
Slag-Phase	PGMs, In(III)	
Fe(II)*	Ni(II), Co(II), Zn(II)	Cu(II), Ni(II), Co(II), Zn(II), Bi(III)
	Cu(II)	
Fe(III)	Re(IV), Sn(IV), Mo(IV)	
	Mo(VI), Sb(V),Te(VI)	
Si(IV)	Se(VI)	Te(VI), As(V), Mo(VI)
	As(V)	
Al(III)	Ge(IV), Te(VI)	Mo(IV), Sn(IV), Re(IV), Sb(V)
*Also occurs as a major element in the matte phase (FeS)		

Predicted miscibilities indicate that Ni, Co and Zn have relatively strong affinities with both the matte and slag forming elements, in the oxide and sulphide phases respectively. These elements can thus be expected to distribute across both the matte and slag phases. Zn compounds are, however, considerably more volatile, and will thus also report to the vapour phase (i.e. Zn will probably occur to a significant extent in all three smelter output phases). The information in Table 8.4 also indicates that the affinity of the chalcophilic elements Se, Te, As, Sb, Mo, and Re for the slag forming elements increases as their ionic charges or oxidation states increase. The deportment of these elements to the slag phase, probably in the form of oxyanions, can thus be predicted to increase relative to the matte phase as the furnace conditions become increasingly oxidising. Oxidation to higher oxidation states will,

however, also have an effect on the element volatilities, and hence their distributions to the vapour phase.

8.2.3 The rate and extent of element volatilisation

Thus far discussions have focused on the properties and behaviours of compounds in terms of their stable form under smelting conditions. The extent to which these compounds report to the vapour phase, relative to the matte and slag phases, will depend largely on the volatilities of these stable forms, as measured by their vapour pressures at typical smelting temperatures.

A plot of vapour pressures for selected elements at 1500K (Figure 8.3) indicates that the vapour pressures of the elements are dependent on both their oxidation states and the forms, sulphides generally being more volatile than oxides. This is moderately so in the case of lead and cadmium; more so in the case of zinc; and significantly so in the case of bismuth, whose oxide is virtually non-volatile.

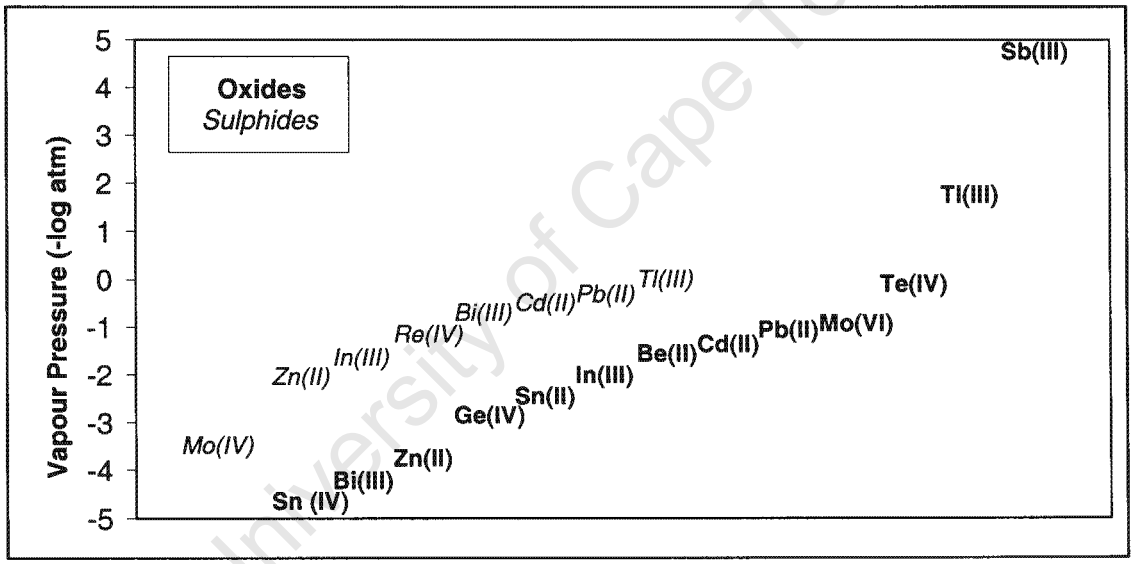


Figure 8.3: Vapour pressures of selected elements at 1500K (See Figure 8.2 for thermodynamic data sources)

Elements are grouped and ranked according to their vapour pressures or volatilities at 1500K, as a function of oxidation state and form, in Table 8.5.

Table 8.6: Qualitative prediction of element distribution behaviour patterns during smelting of copper sulphide concentrates

Elements occurring predominantly in slag phase	
I: Si, Al, K, Ca, Na, K, Mg Ti, Mn, Ba, Rb, Sr, Zr, Li, Nb, Ga, W, B, Ta, Cs, Hf, Sc, Sn.	I Distribution to the slag phase is expected to be extensive under all smelting conditions
II: Be	II Partial distribution to the vapour phase expected under all smelting conditions
III: V, Cr	III: Partial distribution to the vapour phase is expected under oxidizing conditions (volatility of Cr(VI) and V(V))
Elements occurring predominantly in vapour phase	
I P, halides, Re, Tl	I Distribution to vapour phase is expected to be extensive under all smelting conditions.
II Cd> As> Pb> Bi> In> Sb> Zn	II Partial distribution to the slag and matte phase expected, with distribution to vapour phase generally decreasing and to slag phase increasing as conditions become increasingly oxidising.
III Ge, Mo	III Partial distribution to slag phase expected, with relative distributions being dependent on extent of oxidation
Elements occurring predominantly in matte phase	
I Noble metals (PGMs Au, Ag)	I Distribution to the matte phase is expected to be extensive under all smelting conditions
II Se, Te	II Partial distribution to vapour and/or slag phase expected, with distribution to matte decreasing as the smelting conditions become increasingly oxidising
III Ni, Co	III Significant co-distribution to slag phase expected

Consistent with the outcomes of the fundamental assessment, empirical results (see Table 8.1) indicate that, at a copper-matte grade of 55%, nickel is distributed fairly evenly between the matte and slag phases, with deportment to the vapour phase being low to negligible. Empirical results, however, also indicate that nickel distribution to the matte increases, with a corresponding decrease to the slag phase, at a copper-matte grade of 75%. The reasons for this are not clear, as the fundamental studies predict a reverse trend. Cobalt can be expected to exhibit a similar distribution pattern to that of nickel.

At a copper-matte grade of 55%, selenium reports mainly to the matte phase (probably in the form of selenide compounds), although 20% deportment to the vapour phase is also indicative of partial selenide oxidation to the volatile Se(IV) oxide (SeO_2). The distribution of selenium to the matte phase

decreases substantially at a copper-matte grade of 75%, indicating fairly extensive oxidation of selenide compounds under these conditions. A corresponding increase in the deportment of Se to the slag phase is indicative of fairly significant oxidation of selenide to the Se(VI) oxide, which has a lower volatility and a higher affinity with the slag forming minerals than Se(IV) oxide. Tellurium is expected to show similar distribution behaviour patterns to Se, although Te compounds are generally less volatile than those of Se.

Empirical results also indicate that the extent of distribution of elements to the vapour phase decreases in the order As≈ Bi ≥ Pb>> Sb ≈ Zn, at a copper-matte grade of 55%. Such deportment is consistent with the volatilities of the sulphide forms of these elements, indicating that the oxidation of these sulphides is either limited or proceeds at a slower rate than their volatilisation. Empirical results do, however, indicate minor to partial oxidation of these sulphides, with the extent of oxidation and deportment to slag increasing in the order Bi< As ≈ Pb<< Sb< Zn. The higher distribution of Sb and Zn to the slag phase can be attributed to the lower volatilities of their sulphides (relative to those of Bi, As and Pb), as well as the relatively high affinities of their oxide forms, particularly Zn, with slag forming minerals. At a copper-matte grade of 75%, the extents of distribution of As, Bi, Pb and Zn to the vapour phase decrease, with a corresponding increase in the distribution to the slag phase. This is indicative of an increase in the extent and/or rate of oxidation of the sulphides to less volatile As(V), Zn(II), Bi(III) and Pb(II) oxides. Similarly, the observed increase in the distribution of antimony to the vapour phase at the higher Cu-matte grade can be attributed to enhanced formation of the Sb(III) oxide, which is more volatile than the sulphide. The empirical results also indicate partial oxidation of Sb to the Sb(V) oxide, which has a relatively high affinity with the slag forming minerals. The relatively high distributions of Cd to the vapour phase, in comparison to those of As, Bi, Pb and Sb, at the 75% copper matte grade, can be attributed to both the high stability and volatility of the CdS compound. Empirical results also reflect the relatively high volatilities of Hg, and the high affinity of the PGM's, Au and Ag for the sulphide matte phase.

A comprehensive quantitative list of element distributions during matte smelting, based on careful reconciliation of empirical data with a fundamental understanding of the chemistry and associated behaviour patterns of elements under smelting conditions, is presented in Table 8.7

Table 8.7: Quantitative distribution factors for elements during smelting of copper sulphide concentrates

	55 % Cu-matte grade			75% Cu-matte grade		
	Vapour	Matte	Slag	Vapour	Matte	Slag
Hg, *P, Re, Tl*	80-90	5-10	5-10	As for 55 % Cu-matte		
As, Bi, *In*, Pb	All elements: 70-80	10-30	5-10	30-50	10-30	10-30
Cd		10-20	5-10	60-70	10-20	10-30
Ge		5-10	10-30	30-50	5-10	50-60
Sb	All elements: 40-50	30-50	10-30	50-60	30-50	10-30
Zn		10-20	30-50	10-30	10-20	50-70
Mo		5-10	30-50	50-60	<5	10-30
Pt, Pd, Au, Ag	<1	>90	<5	As for 55 % Cu-Matte		
Se, *Te*	10-30	60-80	<5	10-30	30-50	30-50
Ni, *Co*	<1	50-60	30-50	<1	60-70	10-30
Alkali metals Alkaline earth metals *Ti-Hf-Zr-Nb-Ta* *Ga*-Al *Si-B*	All elements: <5	All elements <5	All elements: >90	As for 55 % Cu-Matte		
Cr-V-Sn	5-10	<5	>90	10-20	<5	80-90

Where:

- Distributions are expressed as percent of mass in feed.
- Elements in italics represent those for which no empirical quantitative data is currently available.

8.4 Summary and concluding remarks

The specific aim of this chapter was to demonstrate the applicability of the generalised methodology, as well as the developed understanding and criteria in terms of predicting element distribution during smelting of copper sulphide concentrates, as a function of copper matte grade. As such, this case study serves to highlight the capabilities of the developed methodologies in terms of predicting element distributions in the case of processes entailing relatively complex chemical changes, and to what extent these are influenced by technology choices.

The results of this case study indicate that, although the distribution behaviour of the trace to minor elements will be influenced to a lesser or greater extent by the furnace technology, in general most of the lithophilic elements will report to the slag during smelting of copper sulphide concentrates, whilst many of the less thermally stable chalcophilic elements report extensively to the vapour phase. Trace to minor metals reporting mainly to the matte phase along with the copper include the precious metals, Se, Te and, to a lesser extent, Ni and Co.

Partial deportment of contaminants also occurs to the other smelter outputs to a lesser or greater extent, and may have significant implication in terms of the environmental and eco-efficiency performance of primary copper production operations. As an example, whilst the slag outputs from smelter operations are generally considered to be sufficiently stable for land disposal and/or use in road construction, the deportment of hazardous contaminants such as arsenic and antimony to the slag phase, even though partial (< 30%), could have significant implications, particularly when processing ores containing relatively high levels of such impurities. The potential for adverse effects due to partial element deportment to smelter output streams is likely to be particularly pronounced for operations producing mattes with relatively high copper grades (> 55%), which are generally conducted under more oxidising conditions. The results of this study have indicated the deportment of many elements (particularly the chalcophilic elements As, Bi, In, Pb, Cd and Ge), tends to be more evenly distributed between the slag and vapour phases under such conditions.

Combining the quantitative distribution data presented in Table 8.7 with total mass flow information will enable the generation of a comprehensive inventory list of element concentrations in the primary smelter output streams as a function of feed compositions, as well as furnace technology.

9

Conclusions and Recommendations

This study has developed and demonstrated a systemic risk-based strategy for addressing shortcomings pertaining to information on the environmentally significant characteristics of solid wastes from the primary mineral-based resource industries. The proposed approach developed in this study is underpinned by a qualitative understanding of the solid waste characteristics of key significance in terms of potential environmental risk (i.e. the link between the solid waste properties and associated environmental impacts), as well as the key factors influencing those characteristics in terms of the origins and source of the wastes (i.e. link between feed ores, ore beneficiation processes and solid wastes). This pertains in particular to the mechanisms and parameters controlling the properties, distribution and associations of elements within ore deposits, across process unit operations and, ultimately, from solid waste disposal sites. On the basis of this understanding, generalised criteria, protocols and methodological guidelines for predicting key solid mineral waste characteristics as a function of their origins (ore type) and source (generating process) have been established. Application of the generalised methodologies and criteria has subsequently been demonstrated by means of three separate but inter-related case studies relating to the primary copper production industry sector.

This chapter of the thesis presents the key findings of this study (Section 9.1); highlights the significance of such (Section 9.2); and, finally, concludes with some suggestions for further studies in this area (Section 9.3).

9.1 Summary of key findings

This section presents a discussion summarising the main issues and problems underpinning this study (Section 9.1.1); the key aspects of the proposed approach for addressing these issues (Section 9.1.2); as well as the main observations arising from the case study applications (Section 9.1.3).

9.1.1 The need for a new approach to solid mineral waste characterisation

Chapter 1 of the thesis 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 approach for the prediction of key solid mineral waste characteristics developed from the recognition of three main issues:

1. In order to be effectively managed, potential impacts and risks associated with solid mineral wastes first need to be quantitatively predicted. Without reliable estimation of potential impacts, particularly over the long-term, there can naturally be no meaningful plan to mitigate the 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.
2. The derivation and/or collection of data and information pertaining to the key waste properties or characteristics are, in turn, an essential and integral part of quantitative environmental impact predictions. In particular, the accurate and reliable prediction of the generation of leachate from, and ultimately the environmental impacts associated with, the land deposition of a specific solid waste requires prior knowledge of the environmentally strategic contaminants and their potential behaviour under disposal conditions
3. Currently available data pertaining to the characteristics of solid mineral wastes are largely incomplete and inconsistent, and the mechanisms of leachate generation poorly understood. Furthermore, whilst a vast number of empirical methodologies has been developed for the characterisation of solid wastes, there is a need for a more systematic and informed approach to empirical waste charcterisation.

The motivation for developing a new approach to the characterisation of solid wastes from the primary mineral-based resource industries was thus driven not only by the limitations in terms of current data pertaining to the characteristics of solid mineral wastes. There is also a need to address such shortcomings in a manner which provides decision-makers with key information in the early design stages of a project, whilst simultaneously guiding further data collection and environmental impact prediction studies.

9.1.2 Predicting key environmental characteristics on the basis of waste origins and source

In line with the overarching research objective and hypothesis, Chapter 1 proposed a conceptual hybrid (i.e. semi-empirical/semi-fundamental) approach for addressing data gaps and inconsistencies pertaining to the physio-chemical compositions and environmentally significant properties of solid mineral wastes on the basis of ore characteristics (waste origins) and generating processes (waste source). Whilst the collation of relevant and available data and information forms a necessary first step in the proposed methodology, the approach is largely underpinned by, and relies to a significant extent on, a clear understanding of the key factors governing the properties and distribution behaviours of elements during ore formation, extraction, beneficiation, and, ultimately, waste disposal.

The development of this understanding, together with the subsequent derivation of criteria and generic protocols to support the proposed approach, constituted two of the key research aims, and formed the focus of Chapters 2 to 4 of the thesis. Specifically, Chapter 2 identified the criteria of key significance in terms of potential environmental impact, and developed a generic procedural framework for screening and prioritising solid mineral waste constituents accordingly. This was based on a fundamental understanding of the key factors governing both the hazardous properties and the chemical behaviour (or mobility) of waste constituents under disposal conditions. The application of the developed criteria and protocols for predicting solid mineral waste characteristics of key significance on the basis of hazard potential, chemical mobility and, ultimately, potential environmental risk requires prior knowledge of the compositions of the wastes in terms of both the concentrations and forms of the constituents. Due to their relevance in terms of technical and economic criteria, such as product quality and operational throughput, the distribution 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 are largely qualitative and inconsistent, and their deportment during the formation and subsequent beneficiation of ore deposits generally less well understood. The derivation of meaningful criteria and protocols for the generation of such information was based on a review of the fundamental principles relating to mineralogy, geochemistry, metallurgy and basic inorganic chemistry within Chapters 3 and 4 of the thesis. Specifically, Chapter 3 identified the key factors influencing the enrichment or depletion of elements within certain types of mineral deposits, and grouped elements accordingly. Chapter 4 was concerned with the identification of the key parameters influencing the subsequent distribution behaviour of ore components, and the generic characteristics of the waste outputs, as a function of processing operations and technology options.

Chapter 5 of the thesis was aimed at developing methodological guidelines, supported by a few illustrative examples, in terms of the selection and application of appropriate scientific techniques and

methods for predicting element distribution and process inventory data in accordance with the conceptual approach, criteria and protocols developed within Chapters 1 to 4.

In summary, the generic approach developed for the prediction of key solid mineral wastes characteristics on the basis of origins and source is essentially comprised of two main procedural frameworks, as illustrated diagrammatically in Figure 9.1.

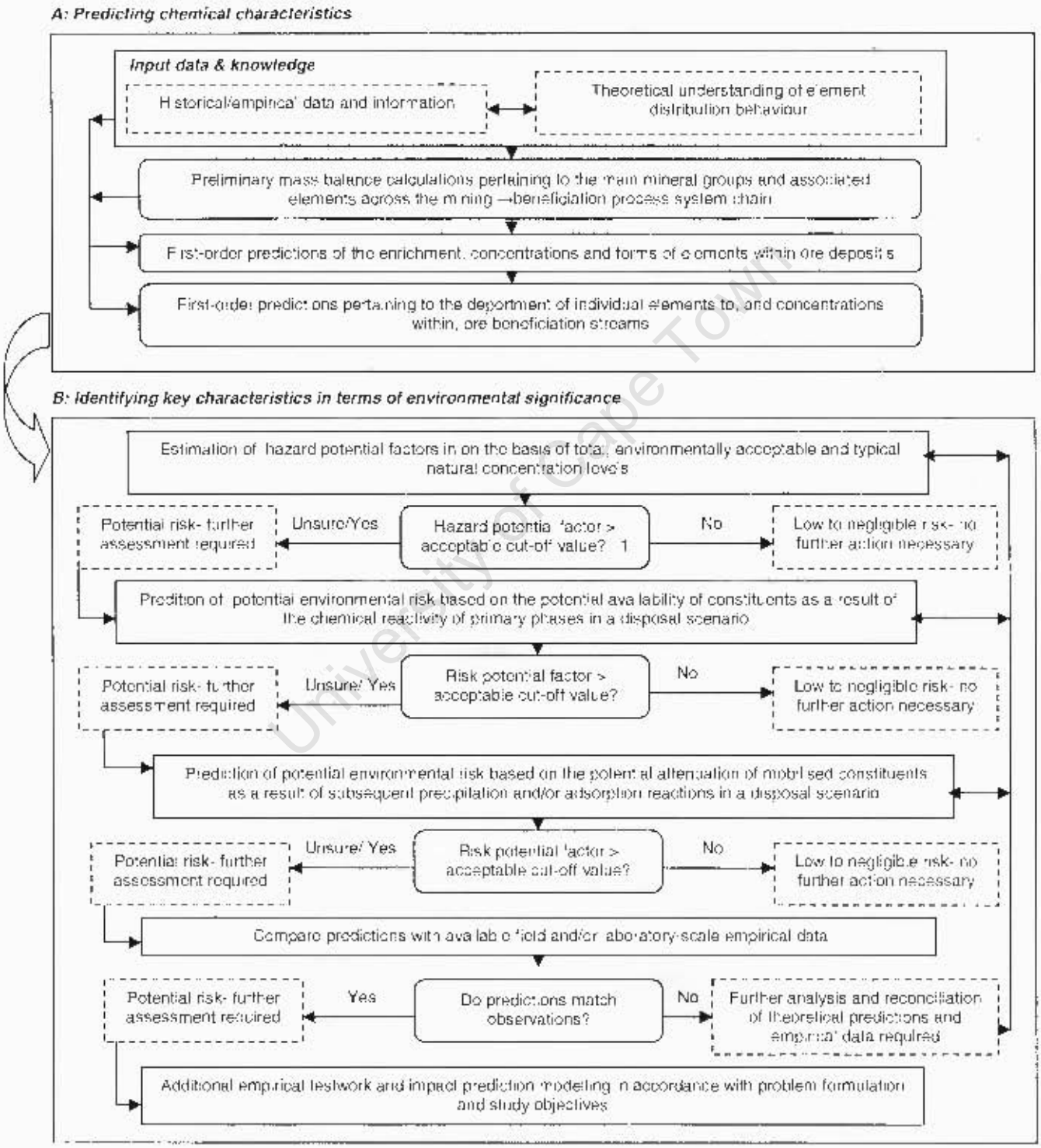


Figure 9.1: Generic procedural framework for the prediction of key solid waste characteristics on the basis of origins and source

In the first instance, data and information pertaining to the chemical composition of solid mineral waste output stream(s) are predicted on the basis of the chemical properties and distribution behaviours of elements during the formation and subsequent beneficiation of ore deposits. The second step entails the prediction of key characteristics relating to criteria of environmental significance i.e. hazard potential and mobility. In accordance with the proposed semi-empirical nature of the conceptual approach, the overarching methodological tasks involved in predicting element distributions and concentration levels within ore formation, beneficiation and, ultimately, waste disposal input-output streams, include:

Task 1: Collation and review of available and relevant empirical data and information for the system under consideration.

Task 2: Theoretical assessment of the distribution behaviour, associations and chemical properties of elements, on the basis of fundamental chemical and thermodynamic principles.

Task 3: Reconciliation of available empirical and theoretical data to generate a comprehensive and quantitative list of input-output stream compositions and/or potential element distribution factors, which can be combined with mass flows to develop mass balance spreadsheets and, ultimately, screen and rank constituents in terms of environmental significance.

These methodological components are comprised of a number of technical elements including flowsheet construction; data collection; analysis & interpretation of empirical data; application of fundamental chemical principles and element periodicity; and predictive thermodynamic modelling as the main scientific techniques. These techniques cover a wide range of scientific disciplines and methods, the appropriate selection and application of which will, in turn, be largely dictated by the relevant criteria, as identified within Chapters 2 to 4 of the thesis, and summarised in Figure 9.2.

In line with the first-order nature of this approach, element concentrations and distributions are expressed as qualitative (e.g. high, medium, low) or semi-quantitative (covering a range of potential values) measures of the typical, rather than absolute, element concentration levels and extents of enrichment, deportment and/or environmental availability (i.e. data quality is consistent with early design stage or screening risk assessment requirements in terms of accuracy and certainty). Whilst the use of detailed and complex scientific techniques and methods for the derivation of such first-order data is thus unlikely to be warranted or meaningful, it has been argued that credibility of the predictions data can be enhanced through the application of a combination of suitable, yet simple techniques, in a manner which allows for validation of the consistency of results.

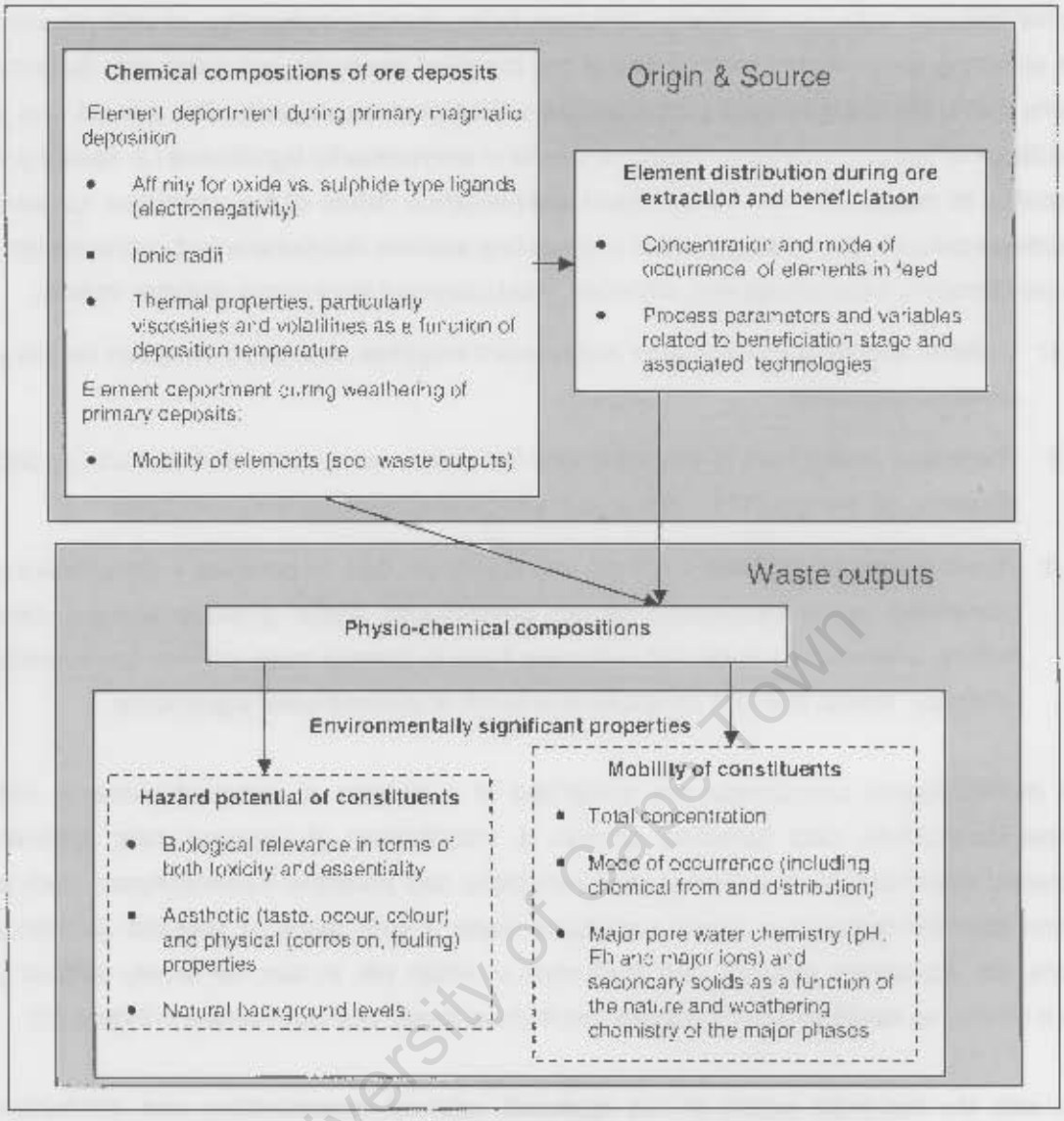


Figure 9.2: A summary of the generic criteria governing element distribution across the ore → beneficiation → waste → environmental impact chain

9.1.3 Observations from the case studies

Chapters 6 to 8 of the thesis demonstrated the application of the generic protocols and criteria developed within the preceding chapters to the primary copper production industry. The selection of this industry sector was based on the fact that it encompasses many of the complexities and problems of relevance to the mineral-based resource industries, including multiple co-elements, complex process flow-sheets, as well as large volume wastes posing a relatively high environmental risk. Three separate but inter-related case studies were designed to specifically demonstrate the key features of the generic rule-based methodology as discussed in the previous section (Section 9.1.2).

Chapter 6 (Case Study 1) focused on the chemical compositions of copper sulphide ore deposits and the subsequent distribution of ore components during early beneficiation by means of milling and

flotation. By reconciling available empirical data and information with a fundamental understanding of the factors influencing element distribution behaviour during the formation, extraction and flotation of generic porphyry-type copper sulphide deposits, a comprehensive inventory list of element concentrations and forms was generated for the ore formation → milling → flotation processing system. Constituents in the tailings output stream were subsequently screened and ranked on the basis of their potential environmental significance under disposal conditions within Chapter 7 of the thesis (Case Study 2). This entailed estimating and comparing the hazard and availability potentials of the various constituents at the generic concentration levels predicted within Chapter 6, thereby highlighting the links in the ore formation → ore extraction & beneficiation → waste disposal → environmental impact causal mechanism chain. Finally, Chapter 8 predicted element distribution during smelting of the copper sulphide concentrate stream as a function of targeted copper matte grade (Case Study 3), thereby highlighting the capabilities of the developed approach and associated tools in terms of predicting element distributions for processes entailing relatively complex chemical changes. This case study also served to highlight the extent to which element distributions during ore processing can be influenced by technology choices on a reactor level.

Whilst the predicted inventory lists are considerably more complete and less dispersed than those compiled on the basis of available historical data alone, levels of uncertainty pertaining to generic data on mineral deposits, and consequently the streams arising from the beneficiation thereof, remain relatively high. 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 case studies provided data and information of key significance in terms of early stage decision-making, as well as further data collection and risk assessment studies in later design stages. In particular, the generic 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 are 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 highly to severely toxic 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 a typical copper sulphide tailings waste stream 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, Case Study 2 (Chapter 7) 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. Case Study 3 (Chapter 8) demonstrated the significant effect that the Cu-matte grade, and associated furnace technology, will have on the relative distributions of many of the co-elements (particularly As, Bi, In, Pb, Cd, Ge and Zn) to the output streams during smelting of copper sulphide concentrates. This case study also highlighted the importance of taking into account the partial, and not only simply the dominant, element deportment

pathways when assessing the compositions of waste outputs in terms of potential environmental significance in a disposal scenario.

9.2 Statement of significance

The ability to generate a comprehensive and, at the same time, comprehensible inventory of process inputs and outputs as a function of ore compositions and processing technology options is likely to have significant benefits for the primary mineral-based resource industries, providing decision-makers with key information in the early design 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. More specifically, the generated inventory data can be used to identify and prioritise potentially strategic constituents[12], as well as to estimate the relative potential for adverse effects (including environmental impact and loss of potentially valuable ore constituents) to occur.

Furthermore, by focusing on, and systematically decoupling, each fundamental step in the causal mechanism chain (ore formation → ore extraction & beneficiation → waste disposal → leachate generation → environmental impact), the approach enables potential environmental impacts to be linked back to the waste management strategies and generating processes themselves. In this way environmental performance can be assessed in response to system changes, thereby facilitating identification of opportunities for process improvements that minimise both the quantities and hazardous nature of the waste outputs - in line with the principles of cleaner production.

The proposed approach is also compatible with the iterative and hierarchical nature of structured decision-making, the importance of which has been highlighted in a key note address (McKee, 2006) delivered at a recent SAIMM workshop on the challenges facing the sustainability of the mineral processing industry. Specifically, the proposed approach takes cognisance of, and assimilates, the requirements and constraints typically associated with early project development phases and process performance assessments, through the use of:

- available data and information as far as is practicable;
- relatively simple predictive techniques and methods;
- qualitative or semi-quantitative measures of element concentration and/or distribution "ranges";
- relative, rather than absolute, measures of potential environmental risk

This ensures that the data and information 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

[12] In the context of eco-efficiency, strategic constituents include those constituents considered to be of key environmental significance (both in terms of their presence in the waste and their impact on the environment) and/or are of significant economic value.

effective. The use of ranges to define input-output streams and performance data is also consistent with the extremely variable nature of natural ore deposits and mineral resource-based process systems.

9.3 The way forward

Whilst the potential overall value of the generalised strategy for predicting the key environmental characteristics of solid mineral wastes has been clearly demonstrated, further expansion and optimisation will increase both the confidence in, and usefulness of, the methodologies and criteria developed within this thesis. 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.

9.3.1 Recommendations for further work

In terms of robustness, the study has identified the poor quality (both in terms of accuracy and detail) of available data pertaining to the parent ore as one of the major limiting factors in terms of the certainty and accuracy of the predicted compositions of the outputs arising from the beneficiation thereof. 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 methodology developed within this thesis. Modern mineralogical analytical methods such as the Mineral Liberation Analyser (MLA) and QEMSCAN™ techniques, in particular, have the potential to generate detailed quantitative data pertaining to the concentrations and modes of occurrence of trace-minor elements within ore deposits, and are already being used fairly extensively to characterise exploration samples and ores ahead of mining and processing within certain industry sectors (see for example recent presentations by de Vaux, 2005 and Theron, 2005). Current industry-related applications and developments in this area are, however, concerned largely with optimising performance in terms of product throughput and recovery. Further work is still required in order to improve the application of the above-mentioned mineralogical techniques in terms of providing data and information for environmental impact predictions in line with the approach developed within this thesis, particularly regarding the reliable quantification of environmentally significant trace-minor phases (< 1000 ppm) and their modes of occurrence within an ore body. 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.

Furthermore, whilst a measure of uncertainty is implied by using data ranges, rather than average or typical values, this study does not address uncertainty explicitly. The application of mathematically rigorous algorithms for quantitative data reconciliation and the measurement and analysis of data

variances will improve transparency of the derived information, and enhance the reliability of the decision-making processes (see studies by Notten, 2001).

Application of the developed protocols and criteria for the prediction of element distribution during the formation and beneficiation of various ore deposits is not a trivial undertaking and requires fairly extensive technical expertise and knowledge. 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 dynamic "expert system" model, which:

(i) Generates and collates 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) Guides the selection and design of beneficiation processes and waste management practices in line with sustainability development principles, as well as further empirical testwork programmes in subsequent process development/project management phases.

9.3.2 Future application of the proposed approach and associated methodologies

The generalised strategy presented in this thesis has been specifically developed to provide information pertaining to the key solid waste constituents of potential environmental significance in a disposal scenario, and is thus compatible with the screening phase of risk-based environmental assessment protocols. However, the strategy also provides a comprehensive, albeit first-order, estimate,of element distribution and input-output concentration data as a function of ore compositions and process technologies. As such, the developed strategy may also find application in the preliminary (in terms of project development) evaluation of potential performance against other sustainability-related objectives and criteria. In particular, the data and information can be used to identify opportunities to improve economic performance of mineral-based resource operations, through the early identification of those trace to minor elements which are potentially valuable, in terms of by-product recovery, and/or undesirable, in terms of product quality and processing penalties.

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