EVALUATION OF THE GEOCHEMICAL AND MINERALOGICAL TRANSFORMATION AT AN OLD COPPER MINE TAILINGS DUMP IN MUSINA, LIMPOPO PROVINCE, SOUTH AFRICA

A master’s research project submitted to the University of Venda, School of Environmental Sciences, Department of Ecology and Resource Management

By

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August 2017

DECLARATION

I declare that “**Evaluation of the geochemical and mineralogical transformation at an old copper mine tailings dump in Musina, Limpopo Province, South Africa”** is my own work, that it has not been submitted before any degree or examination in any other university, and that all the sources used have been indicated and acknowledged as complete references.

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DEDICATION

I dedicate this research work to

The **Almighty God** for His mercy and glory upon me

My mother **Mrs. Thobakgale Stella Mutshinya**

My daughter **Thobakgale Ontlametse ‘Destiny’ Murendi**

And

My beloved family members

For your unconditional love, and installing constant hope in me during the course of my study, I appreciate

ACRONYMS

Al	Aluminium
As	Arsenic
Ca	Calcium
Cr	Chromium
Cu	Copper
CM	Chamber of Mines of South Africa
DME	Department of Minerals and Energy
DMR	Department of Mineral Resources
DWAF	Department of Water Affairs and Forestry
Fe	Iron
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LOI	Loss On ignition
MMSD	Mining, Minerals and Sustainable Development
MPRDA	Minerals and Petroleum Resources Development Act
Ni	Nickel
Ppm	Parts per Million
SANS	South African National Standards
SEM-EDS	Scanning Electron Microscopy-Energy Dispersive Spectroscopy
SO_4^{2-}	Sulphate
WHO	World Health Organization
WRC	Water Research Committee
XRD	X-ray Diffraction Spectroscopy
XRF	X-ray Fluorescence

ABSTRACT

Historically, mining activities have generated vast quantities of abandoned tailings dumps in several regions of South Africa and throughout the world. The management and disposal of huge volumes of tailings dumps has constituted a major challenge to the environment. The current study aims to establish the physicochemical properties and mineralogical characterization of the old copper tailings dump in Musina, to reveal the mobility patterns and attenuation dynamics of potentially toxic or heavy metal species as a function of depth, with a view of assessing their potential environmental impact with respect to surface and ground water systems. This information is crucial in the beneficial utilization of copper tailings in the development of sustainable construction materials as part of reuse approach management system. About twelve tailings samples were collected into polyethylene plastic bags from three established tailings profiles drilled by a hand auger. The collected tailings samples were characterized using standard analytical procedures i.e., X-ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electron microscopy/energy dispersive spectroscopy (SEM-EDS). The transfer of potentially toxic or heavy metal species from tailings to water was evaluated using the standardized batch leaching test (EN 12457) and speciation-equilibrium calculations on the aqueous extracts performed by MINTEQA2. The leachate concentration of cations in the collected tailings samples was determined by inductively coupled mass spectrometry (ICP-MS) and the leachate concentration of anions was determined by ion chromatography (IC).

A modified sequential extraction scheme was applied on the selected tailings samples of the drilled tailings profiles to further understand the mode of occurrence, the geochemical partitioning and distribution, real mobility, and environmental bioavailability of potentially toxic or heavy metal species in the tailings and tailings-soil interface. The extracted fractions or phases from sequential scheme were as follows: (F1) water-soluble fraction, (F2) exchangeable fraction, (F3) carbonate fraction, (F4) iron and manganese hydroxide associated fraction, (F5) organic matter and secondary sulphide associated fraction, (F6) primary sulphide bound fraction, and (F7) residual or silicate fraction. The results obtained from the seven steps sequential extraction scheme were validated by the determination

of percentage recoveries from pseudo-total digestion or total metal content of the original sample. The distribution of major elements and potentially toxic or heavy metal species in different leachate fractions obtained after each step of sequential extraction of the selected tailings samples was determined by inductively coupled plasma mass spectrometry (ICP-MS). The appraised data was used to reveal the impact of atmospheric oxygen and infiltrating rain-water on the chemistry of copper tailings dump by depth profiles.

Macroscopic properties revealed that the abandoned Musina copper tailings are fine to medium coarse grained, and range in color from light/dark gray at the upper or shallow depth of the tailings, to dark reddish-brown at the deeper zone where the tailings are mixed with the underlying soil or soil-interface. The drilled respective tailings profiles were uniform and slightly varied in both mineralogical and bulk chemical compositions with tailings depth. Mineralogical analysis showed the following order of mineralogical composition within the respective tailings profiles: quartz> epidote> chlorite> muscovite> calcite> hematite. Chalcopyrite was the only sulphide mineral observed by optical microscopy, although not identified or quantified by XRD and SEM-EDS analysis. The observed discrete chalcopyrite grains were attributed to the primary mined ore (i.e., chalcopyrite, chalcocite and bornite) during past copper mining activities in Musina. The tailings profiles were characterized by a medium alkaline pH (7.97-8.37) that corresponds very well with the tailings leachates or pore-water pH (8.36-8.46). This pH was constant and slightly varied with tailings depth in the respective tailings profiles. The high abundance of alumino-silicate minerals and traces of carbonates as calcite coupled with low sulphide mineral content, suggested a high neutralization capacity of the tailings which was in common agreement with an alkaline nature of the copper tailings dump. The chemical composition of major elements within the respective tailings profiles followed the order: Si>Al>Fe>Ca>Mg>K>Na, and corresponds very well with the mineralogical composition of the tailings, whereby alumino-silicates were the most abundant minerals in the tailings samples. Nevertheless, the solid-phase concentration of metals decreases with increasing tailings depth as Cu>Sr>Zr>Ni>Zn and was incongruent with the mineralogical composition within the respective tailings profiles. The main secondary minerals were calcite and hematite, and their proportion increased with increasing tailings depth. In addition, hematite formed coatings on the rims and corners of chlorite as observed from optical microscopy, and retained relatively high amounts of potentially toxic or heavy metals (up to 862 ppm of Cu, up to 36 ppm of Ni, and up to 25 ppm of Zn) at the upper and shallow depth of the respective tailings profiles, where bulk density was high and low porosity.

Based on batch leaching tests, the amounts of potentially toxic or heavy metal species released into solution were low (0.27-0.34 µg/L Pb, 0.54-0.72 µg/L Ni, 0.88-1.80 µg/L Zn, and 20.21-47.9 µg/L Cu) and decreases with increasing tailings depth, indicating that, presently, the tailings have a minor impact on heavy metals load transported to the receiving surface and groundwater systems. The low concentration of potentially toxic or heavy metal species in solution is primarily due to their retention by secondary Fe oxide phases (i.e., hematite) and the prevailing medium alkaline pH condition of the tailings leachate or pore-water. The observations are consistent with MINTEQA2 speciation calculations, which predicted the precipitation of secondary phase cuprite (Cu_2O) as the main solubility-controlling mineral phase for Cu, Zn, and Ni. Primary factors influencing aqueous chemistry at the site are neutralization and dissolution reactions as a function of pH, precipitation, and sorption into hydrous oxides (hematite and cuprite).

Based on sequential extraction results, the leachable concentration of potentially toxic or heavy metal species in the water-soluble, exchangeable and carbonate fractions of the respective tailings profiles was relatively low, except for Cu and Mn. For instance, the leachable concentration of Cu and Mn reached 10.84 mg/kg and 321.7 mg/kg at the tailings-soil interface (3 m) in tailings profile C, respectively. The low concentration of potentially toxic or heavy metal species (Cr, Co, Ni, Zn, Cd, and Pb) in these fractions could be due to the low solubility of minerals bearing these trace elements caused by variations in pore-water pH in the respective tailings profiles. The high concentration of Cu and Mn in these fractions suggests their high mobility and therefore most available for uptake in the environment.

Except for Cu>Mn>Cr, the contents of potentially toxic or heavy metal species in the Fe and Mn oxides and organic matter or sulphides bound fractions was low, due to the low

quantity of these fractions in the tailings, despite their high affinity and sorption capacity for potentially toxic or heavy metal species. Likewise, the residual fraction of the respective tailings profiles contained the highest proportion of potentially toxic or heavy metal species. Although the highest potentially toxic or heavy metal species content was in fractions with limited mobility, care must be taken since any geochemical change or shift in the tailings pH or acidic conditions may cause them to be displaced to more mobile fractions, thereby increasing their mobility and environmental bioavailability. Therefore, physicochemical properties of the tailings including pH and mineralogical composition of the tailings samples were the main substrate controlling the geochemical partitioning and distribution, potential mobility, and environmental bioavailability of potentially toxic or heavy metal species by tailings depth. The knowledge of mobility and eco-toxicological significance of tailings is needed when considering tailings dump disposal or reuse in the environment.

The addition of copper tailings at 3 and 28 days successfully improved the compressive strength of cement mortar mixtures incorporating tailings at C5 (5%) and C10 (10%) respectively, although with small margin relative to the control mixture (C0). The maximum strength was 31.15 Mpa attained after 28 curing days, and slightly varied when compared with other compressive strength on copper blended cement mortars mixtures in other countries, used for the development of sustainable construction materials. The chemical composition, physical properties and improved compressive strength on cement mortars mixtures incorporating copper tailings, implies that copper tailings are suitable for the development of sustainable construction materials, thereby ensuring job creation, availability of land for development usage, and the reduction of environmental pollution induced by the abandoned copper tailings dumps.

Keywords: *Copper tailings dump, mobility, bioavailability, potentially toxic elements, sequential extraction, unconfined compressive strength*

Academic output

Presentations and conferences

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Manuscripts being prepared for submission to peer reviewed journal

Thobakgale, R., Gitari, W.M. and Akinyemi, S.A. and Muzerengi, C. **Physicochemical and mineralogical characteristics of the abandoned Musina copper tailings: Implication on the influence of the actual mobilization of potentially toxic elements species within the tailings by depth.** To be prepared for the submission to the South African Journal of Science for Review in 2017.

Thobakgale, R., Gitari, W.M. and Akinyemi, S.A. and Muzerengi, C. **The geochemical partitioning, potential mobility and environmental bioavailability of the potentially toxic elements in various fractions/phases within the tailings and tailings soil-interface.** To be prepared for the submission to the international peer review journal in 2017.

Thobakgale, R., Gitari, W.M. and Akinyemi, S.A. and Muzerengi, C. **The potential beneficial application of dry copper tailings as additives in cement mortar mixtures in the construction industry: Insight on Durability Properties.** To be prepared for submission to the Journal of Engineering Sciences for review in 2017.

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CHAPTER ONE
INTRODUCTION

This chapter gives a brief background on mining activities in South Africa entailing abandoned mines in South Africa, tailings dumps emanating from abandoned mines and their potential environmental impacts, basic concepts of potentially toxic or heavy metal species mobility, release, and attenuation dynamics with regards to surface and groundwater systems. Then, brings the regulation and re-use of tailings dumps disposal. The statement of the problem, research aim and objectives, the methodology that was adopted and thesis structure are also presented.

1.1. Background on mining activities in South Africa

Mining activities involves a series of linked activities whereby the ore deposit is initially probed and outlined from earth materials such as rocks from which commercially valuable mineral resources (copper, gold, or coal etc.) are extracted using an appropriate mining method, either surface or underground mining method (Frenberg, 2007). South Africa has a long history of mining activities dating back from the 19th and early 20th centuries, with the early discovery of gold-bearing conglomerate in 1886 on Langlaagte farm near Johannesburg (CM, 1990). A few years later in 1871 diamond was discovered on the banks of the Orange River and the subsequent exploitation of the kimberlite pipes by De Beers Consolidated Mines (Turrell, 1987). Very soon mining activities in South Africa eventually became pivotal in the country's economic wealth, becoming the leading producer for nearly half of the world's supply of gold and high contributor for dozens of other minerals, such as chrome, copper, manganese, platinum and other base minerals (BRGM, 2001). Nevertheless, the booming of mining activities in the early 1930's and the abundance of minerals in South Africa, spurred interests by many European nations, attracting a huge number of foreign expatriates, foreign investors and labor workers, to contribute to the quick exploitation of discovered mine areas in the country thereby discovering other mine sites (Jones, 2003). However, according to Chamber of Mines of South Africa (1990), by the end of the 1930's the spurred foreign expatriates and investors encouraged state owned enterprises and continued to oppress black entrepreneurs. Nonetheless, in the 1950's and 60's South

Africa was facing fluctuations in the price of gold which left the country's economy unstable, and this economic demise forced government intervention to push for the growth of other manufacturing and agricultural industries which grew rapidly and becoming the largest contributor to the country's GDP by the 1970's (MMSD, 2001). However, it was an unfortunate event for South African citizens since government regulations and Apartheid policies in the 1980's strictly limited the rights of African political, cultural, and economic power to participate in the nation's wealth (DMR, 2001). Nevertheless, during post-Apartheid in the 90's government regulation and policies were revised as an affirmative action empowering the previously excluded black entrepreneurs to participate on the country's economic wealth (Chamber of Mines of South Africa, 2007). Despite the rapid population growth which exceeded economic expansion in the last two decades of post-Apartheid, mining activities in South Africa remained the cornerstone of the country's socio-economy, and today South Africa has the highest mineral wealth compared to any other African country. According to DMR (2009) mining activities in South Africa contributed more than 50 % of the county's GDP in the last 20 years, meanwhile mining employment increased by 9.0 %, moreover mining share of foreign earnings increased to 90 % in the last 20 years. Despite tremendous socio-economic contribution of mining activities in South Africa, unsustainable mining activities resulted on abandoned mine operations whereby the owners left without trace. Waste dumps such as mountains of ore stockpile, waste rock and tailings dumps emanating from abandoned mines may cause adverse environmental changes or impact in various ways (Oelofse, 2007).

1.1.1. Abandoned mines in South Africa

Abandoned mines are certainly defunct mining operations whose owners or lease holders have abandoned and are not operating or sustaining the associated health, safety, and environment during post-mine closure (DMR, 2009). The mine operation is likely to be abandoned by the operators possibly because of low level of productivity, inefficiency in the exploitation and mineral processing of the product (MMSD, 2002). As a result of South Africa's long history of mining activities, the country has many abandoned mines that are currently the major source not only for environmental but also financial and social problems (Matshusa and Makgae, 2014). In South Africa about 6000 mine operations have been abandoned by their operators, with little or no regard to the management of the health, safety and environmental impacts, and this becomes the responsibility of the government to practice post-closure management using public funds (DMR, 2009). However, the large number of abandoned mines in South Africa comprise of mines that operated before or during the 1950’s when environmental management practice was not regulated (DMR, 2006). During the 1950’s the legislation framework developed prescribed only the safe-making of operations i.e., Mines, Works and Machinery regulations (Pulles, 1992). Nonetheless, during the 90’s and post-Apartheid era the legislation framework was revised, introducing new policies that give rise to society and environmental awareness. For example, the Mineral Act 50 of 1991 was the first piece of the revised legislation framework to prescribe more comprehensive environmental management and rehabilitation which include providing sufficient finance for rehabilitation during post-mine closure, at the commissioning stage of mining (DMR, 2009). The current legislation of the Minerals and Petroleum Resources Development Act (MPRDA) corroborate as this legislation provide some guidance mine closure process which depicts that mines are only regarded as closed when the closure certificate is issued in terms of section 43 of the MPRDA (DMR, 2006).

However, abandoned mines have been reported to have adverse negative impacts on the health and safety of local and remote communities and the surrounding environment (Matshusa and Makgae, 2014; Mhlongo and Dacosta, 2015). Potential environmental impacts induced by abandoned mines may include disturbance of valuable land and vegetation destruction, radioactive windblown dust from dried-out tailings and heavy metals leaching with the potential of triggering acid mine drainage from tailings dumps and ore stockpiles emanating from abandoned mines, giving rise to changes in air quality, surface, and groundwater contamination (DMR, 2009). The duration of these environmental impacts can be long-term, for example many areas along the Vaal and Orange Rivers were mined a century ago and the environmental footprints are still prevalent (WRC, 2004).

1.1.2. Tailings dumps emanating from abandoned mines

Abandoned mines are a consequent of non-regulated past mining activities, and tailings dumps are their major physical feature (Matshusa and Makgae, 2014). However, waste such as ore stockpile pile, waste rock and open shafts also form part of the physical features of abandoned mines (DMR, 2009). Tailings are generated from the exploitation of mineral resources during mining activities, and are disposed on land-fills in an impoundment as tailings dumps (Hiller *et al*. 2013). Tailings dumps contain un-economic minerals, potentially toxic or heavy metals (Cu, As, Ni, Zn), inorganic chemicals used during mineral processing, and have been reported to occupy large hectares of valuable land that can be used for development project ensuring employment generation and heritage areas (Lottermoser, 2010). Tailings dumps disposal pose a threat to valuable land as may result on vegetation destruction with the potential of soil erosion, and the high concentrations of heavy metals can cause the soil nutrients to be unsuitable for the growth of agricultural production. For example, high copper (Cu) concentration was reported to be 789 ppm at the abandoned copper tailings dump in Musina, exceeding the Canadian soil quality guidelines for industrial use (1999).

Moreover, approximately 270 gold tailings dump disposal are found in the Witwatersrand basin in Johannesburg and covers an estimated surface area of about 400 km^2, the abandoned copper tailings dump in Musina covers an estimated surface area of around 4.99 km^2, meanwhile the abandoned cassiterite tailings dump located at the eastern limb of the Bushveld complex in Mokopane covers an estimated surface area of around 3.9 km^2 (Anglogold Ashanti, 2004). This just shows how valuable land is covered and disturbed by tailings dumps disposal, land that can be used for welfare, heritage and agricultural production. Tailings dumps disposal not only occupy and disturb large valuable land, but also represent a potential risk for the aquatic system through the release of potentially toxic or heavy metals and metalloids occurring in a variety of minerals present within the tailings dumps disposal (Sracek *et al*. 2010; Romero *et al.* 2007; Moncur *et al*., 2005). The sulphide minerals (mainly pyrite) present within the tailings are susceptible to oxidative weathering, and when exposed to atmospheric oxygen in the long term and infiltrating rain water may result in the formation of acid mine drainage with low pH acidic conditions laden with high concentrations of sulphates (SO_4^{2-}), and potentially toxic or heavy metals and metalloids (Rice and Herman, 2012). Under low pH conditions, many potentially toxic or heavy metal species (Cu^{2+}, Zn^{2+}, and Ni^{+}) are generally more soluble and mobile than in near-neutral pH conditions (Conesa *et al.,* 2008). Consequently, this may contaminate the receiving surface and groundwater systems, causing changes to local groundwater dynamics in terms of both quantity and quality of water and its flow direction, and loss for aquatic habitat and the establishment of alien invasive species (MMSD, 2001). Groundwater in the mining district of Johannesburg in South Africa is heavily contaminated with potentially toxic or heavy metals and acidifies as a result of oxidative weathering of pyrite present within the mine tailings dumps (Naicker *et al*. 2003).

However, this is mainly due to the absence of minerals in the tailings dumps that are able to neutralize the acidity generated by sulphide oxidation (Hiller *et al*. 2013). According to Bortnikova *et al*. (2012), the main minerals within the tailings dumps, decreasing the acidity, are carbonates such as calcite, dolomite, siderite, and alumiono-silicates such as chlorite, epidote, and plagioclase. Neutralization of the acidity in the tailings occurs through the dissolution of these carbonate and alumino-silicate minerals which consumes hydrogen ions and generates neutral conditions within the tailings systems and consequently, dissolved concentrations of potentially toxic or heavy metal species in tailings leachates and pore waters are relatively low (Romero *et al*. 2007).

Nevertheless, considering the large hectares of land occupied by tailings dumps disposal and their potential environmental pollution, a strong regulatory framework is suddenly required to ensure that mine development, including post-mine closure do not result in the destruction of the surrounding ecosystems ensuring the health and safety of the environment. According to the Health and Safety Act, 1996 (Act 29 of 1996), the Department of Minerals and Energy (DME) currently known as the Department of Mineral Resources (DMR), is involved in the administration of mining pollution control and waste management (DWAF, 1997). However, the major risk of mine pollution is likely to arise after mine closure, when mountains of tailings dumps and ore stockpiles are carelessly left abandoned (Lottermoser, 2010). Most of the tailings dumps found within the

Witwatersrand basin were generated by mines that have operated and closed before the 1950's when environmental management practice was not regulated, meaning this becomes the responsibility of the government to administer pollution derived from these mines with the use of public funds. However, the mines that operated and closed after the 1970's and those that are currently operating may be of less concern in terms of pollution risk because of the current legislation framework of the Minerals and Petroleum Resources Development Act (MPRDA) that prescribe a more comprehensive environmental management and rehabilitation, which include providing sufficient finance for rehabilitation during mine development and post-mine closure (DMR, 2009). Nevertheless, tailings management in South Africa is regulated by law in the guideline for the compilation of a Mandatory Code of Practice on Mine Residue Deposits issue by the Department of Minerals and Energy in 2000, currently known as the Department of Mineral Resources (DMR). This guideline makes the implementation of a code of practice mandatory for each tailings facility with compulsory adherence to the South African National Standards (SANS) 10286, code of practice for Mine Residue Deposits (Anglo, 2005).

Moreover, the Department of Mineral Resources (2009) reported that there are three main approaches that could be considered for mineral waste management, and these include rehabilitation, recovery, and re-use. According to Godfrey *et al*., (2007), varying policies drive these approaches; rehabilitation: driven by environmental policy to ensure that tailings dumps disposal and stockpiles pose a minimal threat to the environment and human health. Recovery: driven by economic policy to ensure optimum use of the country's natural resources by a cost-effective and competitive mining industry, and reuse driven by integrated pollution and waste policy to ensure that waste is firstly reduced, then reused and recycled, with disposal seen as last resort.

However, so far, a few researchers and some private companies considered tailings management approach aiming to rehabilitate, recover and re-use tailings dumps disposed on land in the country (Mhlongo and Dacosta, 2015; Matshusa and Makgae, 2014; Engineering and Mining Journal, 2008). In terms rehabilitation and recovery, it is reported that Anglogold Ashanti's East Rand Gold had processed 890 million tons of tailings to produce 8.2 million ounces of gold and uranium (Engineering and Mining Journal, 2008). Nevertheless, in terms of re-use approach a market must first be identified to put tailings dumps disposal in good use. Many researchers have recently identified the construction industry as the best re-use market for tailings dumps disposal with considerable success (Onuaguluchi and Eren, 2012; Mahmood and Mulligan, 2007). Mahmood and Eren (2012) investigated the use of copper mine tailings for unpaved road basement, Ahmari and Zhang (2012) investigated the feasibility of utilizing copper mine tailings for production of eco-friendly cement-less bricks through geopolymerization technology, Mahmood and Mulligan (2007) investigated the blending of copper tailings with other raw materials in the production of unglazed tiles.

The re-use approach management system for tailings dumps disposal proved to be cheap, cost effective, environmental friendly and minimize waste byproducts on the previously usurped land. However, prior to the re-use approach management system for tailings dumps disposal, it is necessary to establish the geochemical and mineralogical characterization of tailings dumps disposal (Lottermoser, 2010). As such, the present study aims to evaluate the physicochemical properties and mineralogy of the old copper mine tailings dump in the township of Musina in order to assess its current state on the potential release of potentially toxic or heavy metal and metalloids species with regards to surface and groundwater systems, and determine the suitability of tailings dumps disposal for development of sustainable construction materials as part of re-use management approach system.

1.2. Statement of the problem

South Africa has a long history of mining activities dating back a century ago, resulting on the generation of large volume of tailings disposed on landfills as tailings dumps (DMR, 2009). Generally, tailings dumps contain un-wanted and un-economic minerals, potentially toxic or heavy metal and metalloids (Cu, Pb, Zn, Co, Ni), and inorganic chemicals such as sulphuric acid used to enhance ore separation during mineral processing (Lottermoser, 2010). However, tailings dump disposal have been reported to occupy large hectares of valuable land that can be used for development projects ensuring employment generation, for example most of the gold tailings dumps are within the Witwatersrand basin in Johannesburg and occupy an estimated surface area of 200 km^2, the abandoned copper mine tailings dump located in Musina occupy an estimated surface area of about 4.99 km^2 (Godfrey *et al*. 2007). Furthermore, tailings dump disposal not only disturb valuable land but also a major source of environmental pollution on surface and groundwater systems, through the release of potentially toxic or heavy metal and metalloids occurring in a variety of minerals present within the tailings (Hiller *et al*. 2013). Sulphide minerals (mainly pyrite) present within the tailings dumps are susceptible to oxidative weathering when exposed to atmospheric oxygen in the long-term and infiltrating rainwater, resulting in drainage water with low pH or acidic condition laden with high concentrations of sulphates and potentially toxic or heavy metal and metalloids species, consequently this may contaminate the receiving surface and groundwater systems (Romero *et al*. 2007). The release of potentially toxic or heavy metals from disposed tailings dumps may be persistence for years thereby affecting the entire ecosystem, and is mainly due to the absence of minerals such as carbonates and alumino-silicates in the tailings that are able to neutralize the acidity generated by sulphide oxidation (Rice and Herman, 2012).

However, in terms of mineral waste management, the Department of Mineral resources (2009) issued three management approach system for tailings dumps disposal, and these include rehabilitation, recovery, and re-use. Furthermore, the re-use approach management system for tailings dump disposal proved to be cheap, cost effective, environmental friendly and minimize waste byproducts on the previously usurped land.

However, prior to the re-use approach management system for tailings dump disposal, it is necessary to establish the geochemistry and mineralogical characterization of tailings dump disposal in order to assess its current environmental state (Lottermoser, 2010). In South Africa, much of the previous work done on abandoned copper tailings dumps disposal focused on mineralogical characterization (Ekosse *et al.* (2004), assessment of heavy metal pollution on soils adjacent to the abandoned copper tailings dumps (Singo, 2013), and geochemical fractionation of metals within the abandoned copper tailings dumps (Gitari *et al*. 2016). Nonetheless, the challenge is to understand the extent of mineralogical transformations, geochemical partitioning and real mobility, and the potential environmental bioavailability of potentially toxic or heavy metals released from tailings dumps disposal in South Africa. This is very crucial when conducting tailings dumps disposal management systems, and when exploring the suitability of copper mine tailings dumps as suitable construction materials. In the present study, the application of sequential extraction scheme, mineralogical evaluation, and batch leaching tests will serve as techniques to determine the physicochemical properties of the old copper mine tailings dump and elucidate the natural attenuation dynamics of the released potentially toxic or heavy metals within the disposed tailings dumps. The unconfined compressive strength tests will serve as a technique to plan a potential beneficial application of copper mine tailings dumps disposal and ensuring sustainability within the construction industry.

1.3. Aims

The research aims to evaluate the physicochemical properties and mineralogy of the old copper mine tailings dump in order to elucidate the attenuation dynamics of potentially toxic metal and metalloids species, and determine the suitability of tailings dump disposal for development of sustainable construction materials.

1.4. Specific objectives

- To determine the mineralogical assemblage and bulk chemical composition of the abandoned copper tailings by depth and tailings soil-interface;
- To identify the physicochemical and mineralogical processes in the tailings that control the mobility/sinking of potentially toxic metal species;
- To evaluate the geochemical partitioning of major and trace elements in the tailings by depth and tailings soil-interface;
- To evaluate the potential mobility/bioavailability of the potentially toxic elements within the tailing deposit by depth and within the tailings-soil interface, and
- To determine the suitability of the copper mine tailings for development of sustainable construction materials

1.5. Key research questions

- ➢ What are the physicochemical properties of the tailings and how do they influence the actual mobilization of potentially toxic metal and metalloids species within the tailings by depth and tailings soil-interface?
- ➢ What are key geochemical processes that govern the partitioning of elements in various geochemical phases of the tailings dump?
- ➢ Is the metal and metalloid species mobile and bioavailable in the tailings of concern to the environment, with respect to surface and groundwater resources contamination?
- ➢ Can tailings dump be suitable for sustainable construction materials?

1.6. Hypothesis

To understand toxic metal species mobility and attenuation dynamics of tailings material and its suitability for sustainable construction materials, a thorough understanding of the various physicochemical forms, identification and quantification of those phases is required.

1.7. Scope and delimitations of the study

In this study, the physicochemical properties and mineralogical transformation was investigated at an old copper mine tailings dump located at the township of Musina in Limpopo Province, South Africa. Three tailings profiles were established with the use of a hand auger driller, namely tailings profile A, B and C. Tailings profiles A and B were drilled to depths of 5m respectively, while tailings profile C was drilled to a depth of 3m. In total, 12 samples were procured from the established tailings profiles, and prepared within the laboratory for mineralogical and geochemical analysis with standard analytical techniques. The obtained data was appraised to evaluate the physicochemical properties and mineralogical changes within the tailings such as total concentrations of total elements, pH and Eh, primary and secondary minerals, in order to elucidate the natural attenuation dynamics of potentially toxic or heavy metals within the tailings by depth. Moreover, the unconfined compressive strength test was applied on the procured tailings samples and the obtained data was used to determine the suitability of copper mine tailings dumps disposal for development of sustainable construction materials.

However, the delimitations of the present study should be clearly spelled out. Although three tailings profiles were established and drilled, tailings profile B and C were considered meanwhile profile A was considered as a control for all the analysis performed. This was mainly due to the uniform character (mineralogical and chemical composition) of the drilled tailings dump. A modified sequential extraction scheme was only applied to the selected tailings to eliminate too much data and cost constraints. Unconfined compressive strength tests were only conducted on the tailings samples for only 3 and 28 days, respectively due to of time constraints and the availability of instruments. However, it is hoped that this study, although focused on the specific site system, will be of benefit to other researchers investigating the geochemistry and mineralogical transformation at abandoned mine dumps and their possible impact on the environment worldwide.

1.8. Research approach

The physical characterization which include, the determination of bulk density, air-filled porosity, and moisture content and specific gravity was performed in the laboratory. The Bulk density was determined on air-dried samples using gravimetric technique, from which air-filled porosity was calculated. The initial moisture content was determined according to ASTM D 2216 (1998). Specific gravity was also performed at the laboratory according to ASTM D 854 (1998). The chemical characterization of the tailings was performed on the respective tailings profiles, and this included the determination of chemical elemental composition of the tailings, pH and Eh by tailings depth. The chemical elemental composition of the tailings was determined by XRF. The tailings pH and Eh were determined from a paste with the use of a combined *Thermo Scientific* instrument. Mineralogical characterization was performed on the tailings samples by XRD, SEM-EDS, and optical microscopy. The data generated from these analytical techniques appraised the potential risk by the heavy metals locked in the copper tailings pose to the surface and groundwater systems in the vicinity of the dump.

The pH, EC and TDS parameters were measured on pore water of the tailings samples. The water-soluble element species in the pore water was determined by ICP-MS and the anion species in the extracted pore water were determined by IC. The data generated from pore water chemistry was appraised to simulate the impact of atmospheric oxygen and infiltrating rain water on the chemistry of the tailings samples. Sequential extraction scheme was applied to identify various geochemical phases hosting the heavy metals and quantify to determine the mobility and environmental bioavailability of potentially toxic or heavy metals and their potential toxicity on surface and groundwater systems. The sequential extraction method used in this study was modified from that of Tessier *et al.* (1979) and Dold (2003) with the addition of the water soluble fraction. The following seven extraction scheme was used in the present study: (a) Water-soluble fraction, (b) Exchangeable fraction, (c) Carbonate fraction, (d) Reducible or Fe and Mn and hydroxide associated fraction, (e) Organic and secondary sulphide fraction, (f) Primary sulphide fraction, and (g) Residual or silicate fraction. The chemical reagents used were specific for each extraction to avoid the attack of other phases or fractions. The results obtained from the seven steps sequential scheme were validated with the determination of total metal content of the original sample. The data generated from sequential extraction for the respective drilled tailings profiles was used for statistical analysis to understand the relationship between species, their behavior and mobility controlling physicochemical factors. Statistical analysis was done using SPSS statistical software, whereby the relationship between species was assessed by cluster analysis, factor analysis was used to assess the main geochemical processes controlling investigated species at different fractions by depth, and principal component analysis was used to assess the similarity in the chemical composition of the tailings samples.

Unconfined compressive strength tests were conducted on the tailings dumps, and the obtained data was used to propose a potential beneficial application of the abandoned copper tailings dumps as part of environmental remediation strategies. In this case, three mix designs were prepared respectively, to be tested for the compressive strength in 3 and 28 days. The mix designs were prepared according to ASTM C 109 (2008). However, the mix design was, the control mix or normal cement mix (Co), mix 2 incorporating 5 % of tailings by addition level (C5) and mix 3 incorporating 10 % of tailings by addition level (C10). The prepared mix designs were subjected to an unconfined compressive test machine and the obtained compressive strength was compared with the normal cement mix for 3 and 28 days, respectively.

1.9. Thesis layout

This thesis is structured into seven chapters:

- Chapter one introduces brief background on mining activities in South Africa entailing abandoned mines in South Africa, tailings dumps emanating from abandoned mines and their potential environmental impacts, basic concepts of potentially toxic or heavy metal species mobility, release and attenuation dynamics with regards to surface and groundwater systems. Then, brings the regulation and re-use of tailings dumps disposal. The statement of the problem, research aim and objectives, the methodology that was adopted and thesis structure are also presented.

- Chapter two provides a conceptual framework of the study. This is followed by a general literature review on mining activities in South Africa, mine waste including tailings dumps, a review on physicochemical characteristics of tailings dumps, and geochemical processes governing the mobility of potentially toxic or heavy metal species within tailings dumps, the possible impacts of potentially toxic or heavy metal species on aquatic systems and the suitable application of tailings dumps disposal for the development of sustainable construction materials. A review on sequential extraction scheme is also presented.
- Chapter three gives an overview on the study area, conceptual framework and insight on the research methodology. The research methodology is divided into field work, laboratory work, and data analysis or results presentation.
- Chapter four provides experimental results obtained from the determination of the physical characteristics of the tailings and analytical results obtained from mineralogical and chemical characterization of the tailings dump.
- Chapter five present experimental results obtained from the application of the sequential extraction scheme modified after Tessier *et al*. (1979) and Dold (2003) for the speciation of particulate trace metals in different geochemical fractions. The geochemical partitioning, mobility, and potential environmental bioavailability of potentially toxic or heavy metals within the tailings by depth and within the tailings soil-interface will be elucidated.
- Chapter six present experimental results obtained from the determination of the unconfined compressive strength on three mix design incorporating the addition of tailings by mass curing at 3 and 28 days respectively. The obtained results crucial on determining the suitability of tailings dumps disposal for development of sustainable construction materials, as part of management system approach on tailings dumps disposal.

- Chapter seven provides a summary of the main findings of the thesis, conclusions, and recommendations to be implemented for future research.

CHAPTER TWO

LITERATURE REVIEW

This chapter provides a conceptual framework of the study. Subsequently, the discussion on mining activities in South Africa, mine waste (mine waters, waste rock and tailings) generation, disposal and environmental implication, physicochemical characteristics of tailings dumps and natural attenuation dynamics, metal speciation and overview of sequential extraction scheme, and the utilization of tailings dumps in the construction industry.

2.1. Conceptual framework

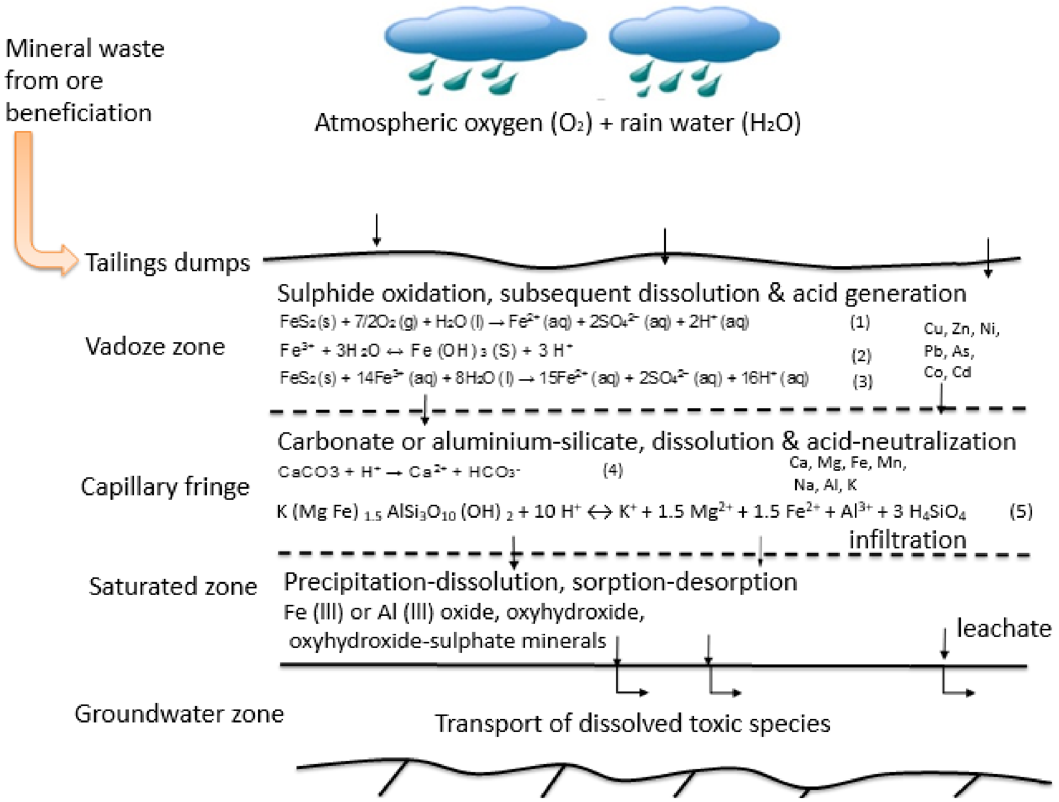


Fig.2.1: Conceptualization of the characteristic barrier zones and geochemical mechanisms which occur within tailings dumps.

Historically, the lack of regulatory enforcement on mining activities have resulted in the distribution of abandoned mine sites, in South Africa and throughout the world (Matshusa and Makgae, 2014). The distribution of abandoned mines pose a challenge and threat to the surrounding environment as they are characterized by large volume of inactive or abandoned tailings dumps occupying hectares of land. Some of the abandoned tailings dumps in South Africa include the abandoned copper tailings generated from past copper mining in Musina, the abandoned gold tailings generated from the abandoned Birthday Gold mine at Giyani and Witwatersrand basin in Johannesburg, and the abandoned cassiterite tailings generated by the abandoned cassiterite mine at the Northern limb of the Bushveld Complex in Mokopane (DMR, 2009).

Although, abandoned tailings dumps vary accordingly on the type of the ore mined and mining equipment used, mineralogy and geochemistry, chemicals implemented during mineral processing, and particle size, however they do constitute common potential environmental pollution sources, because of the oxidation and subsequent dissolution of minerals present within the tailings (Lottermoser, 2010). In a sulphidic mine tailings, the sulphide minerals (mainly pyrite) present within the tailings are very reactive and unstable, and susceptible to oxidative weathering, mainly when exposed to atmospheric oxygen and infiltrating rain water (Hiller *et al*. 2013). Consequently, leading to the generation of acidic leachate effluent in the vadoze zone (unsaturated zone), usually containing high concentrations of dissolved potentially toxic or heavy metal and metalloids species (Cu, Zn, Pb, Co, Cr, Ni), and sulfates (SO_4^{2-}) (Fig. 2.1).

Sulphide oxidation may be extensive, and the acidic leachate effluent (laden with potentially toxic or heavy metal and metalloids species, and salts) may contaminate ground and surface water, soils, and sediments, thereby affecting the entire ecosystem (Joeng, 2003). However, in tailings dumps, acid generating minerals (sulphide minerals) often occur in close association with potential acid-neutralizing minerals (carbonate or alumino-silicates). When sufficient acid-neutralizing minerals are present in the tailings, the acid generated by sulphide oxidation is neutralized in the vadoze zone (Fig. 2.1). Neutralization of the acidity occurs through the dissolution and precipitation of carbonate or alumino-silicate minerals present within the tailings dumps, which consumes the hydrogen ions generated during sulphide oxidation (Blowes, 2003). Consequently, the dissolved concentrations of potentially toxic or heavy metal and metalloids species in tailings leachates and pore waters eventually become relatively low at the saturated zone (Fig.2.1).

Nevertheless, the dissolution of carbonate or alumino silicate minerals release alkali earth and base cations, including Ca, Al, Mg, Fe, Na, K, and Mn, which may precipitate resulting on the formation of secondary mineral phases at the saturated zone (Fig.2.1). The precipitated secondary mineral phases may include Fe (lll) or Al (lll) hydroxides, oxyhydroxydes, and oxyhydroxide-sulphates in the saturated zone (Romero *et al*., 2007). However, the formation of secondary mineral phases plays an important role on the mobility and attenuation of dissolved potentially toxic or heavy metal and metalloids species, through adsorption and co-precipitation under certain geochemical conditions (Blowes *et al*. 2003). This has shown to be an important geochemical process retaining the oxidation products before percolating water reaches the groundwater zone, and therefore moderating the severity of potentially toxic metal and metalloids species on the environment with regards to aquatic systems.

2.2. Mining activities in South Africa

Mining is a process whereby commercially valuable mineral resources are extracted from earth materials such as rocks (BRGM, 2001). Once the ore deposit is probed and outlined and is of sufficient quality to justify mining, the process of selecting an appropriate mining method will commence. According to Lottermoser (2010), a selected mining method can be an underground or surface mining method. South Africa has a long history of mining activities dating back from the 18th century, with the early discovery of gold-bearing conglomerate in 1886 on Langlaagte farm near Johannesburg, followed by the discovery of diamond on the banks of the Orange River (Turrell, 1987).

Mining activities in the country eventually became pivotal to the country’s economic wealth. Consequently, attracting a huge number of foreign expatriates and foreign investors to contribute to the quick exploitation of discovered mine areas (MMSD, 2001).This vast acceleration in the 20th century contributed to the discovery of other mineral deposits including copper, coal, gold, manganese, chrome, iron ore, platinum group metals, vanadium, vermiculite, and titanium (DMR, 2001). These commodities are essentially produced by major companies such as Rio Tinto, Anglo American, De Beers, Exxaro, BHP Billiton, Goldfields, and Rand Mines.

According to MMSD (2001), the substantial expanding mining activities in South Africa was accompanied by the development of infrastructure including the construction of schools, tertiary institutions, railways and roads, and the development of agriculture and establishment of manufacturing industries. The Limpopo Provincial Government (2012) corroborates by reporting that Exxaro has spent approximately ZAR 140 million on community developments in Limpopo, while De Beers South Africa established a skills development center linked to its Venetia mine for both the mine employees, local schools and the adults learning center for the community of Alldays town.

However, unsustainable mining activities could have devastating impact on the surrounding environment during post closure or when the mine is abandoned. When large volumes of mine waste including tailings emanating from abandoned mines are unsustainable, they occupy and disturb the surrounding environment (Lottermoser, 2010). Most of the mines which operated in the 19th century are now closed and owners are untraceable, hence post closure management becoming the responsibility of the government (DMR, 2009). DMR (2009) further reported that operating mining companies today are however, legally responsible to manage their mine waste to alleviate the negative impact that may be caused on the surrounding mining environment.

Moreover, the Department of Mineral Resources (2009) discovered about 6000 ownerless derelict or abandoned mine sites including mine tailings dump, with little or no regard to the management of impacts on public health and safety and the environment. This situation is more acute in regions of the world, where abandoned mines are close to human settlement, and may pose a threat to the people due to high concentrations of metals leaching from tailings material (Matshusa and Makgae, 2014).

Moreover, the situation of abandoned mines may pose enormous financial and social challenges especially on adjacent poor communities. As such, it is necessary to establish the geochemical and mineralogical transformation in the abandoned mine tailings, as this information is relevant in selecting an appropriate rehabilitation method, reclamation for future land use, and investigate the suitability of mine tailings for potential beneficiation application in the construction industry. This information will be crucial on tailings environmental remediation as pertains to aquatic systems.

2.3. Mine waste

Mining, mineral processing, and metallurgical extraction produce solid, liquid and gaseous wastes (Lottermoser, 2010). Moreover, Lottermoser (2010) reported that these mine wastes can further be classified as solid mining, processing and metallurgical mine wastes and mine waters.

2.3.1. Solid mining waste

Solid mine waste are heterogeneous sub-economic geological materials and may consist of sedimentary, metamorphic, or igneous rocks, soils and loose sediments (Ayres, 2002). As a consequence of transport costs, these materials are placed in large heaps in the immediate vicinity of the main mining center (BRGM, 2001). However, solid mining wastes ranges in particle sizes from clay size particles to boulder size fragments (Lottermoser, 2010). According to BRGM (2001) solid mining waste either does not contain ore minerals, metals, or the concentration of the minerals, or include waste rocks, overburden, and ore stockpiles excavated and mined from surface and underground mining activities.

Lottermoser (2010) further reported that the physical and mineralogical characteristics of solid mining wastes vary according to their mineralogy and geochemistry, type of mining equipment, particle size of mined material, and moisture content. However, the primary sources for these materials are rock, soil and sediment from surface mining operation, especially open pits, and to a lesser degree rocks removed from underground workings (BRGM, 2001).

2.3.2. Processing mine waste

Once the ore is mined using appropriate mining methods, it is then processed through beneficiation or mineral processing to physically treat and separate the ore prior to any metallurgical operation (Lottermoser, 2010). Mineral processing techniques may include simple washing of the ore, gravity, magnetic, electrical or optical sorting, and addition of processed chemicals to the crushed and sized ore in order to aid separation of the sought-after minerals from the gangue during flotation (Ripley *et al*. 1996).

These mineral treatment methods result in the production of processed waste (Fig. 2.2). Consequently, processing wastes includes tailings, sludge, and waste water from mineral processing (Ripley *et al*., 1996). However, according to Lottermoser (2010), the physical and chemical characteristics of processing wastes vary according to the geochemistry and mineralogy of the treated ore, type of processing technology, particle size of the crushed material, and the type of process chemicals added during separation. In contrast to solid mining waste, the particle sizes for processing wastes can range from colloidal size to coarse and gravel size particles (Blowes, 2003).

Nevertheless, processing waste is usually deposited as sediment slurry at the surfaces adjacent to the mine workings into a constructed or designated impoundment (Lottermoser, 2010). Processing mine waste can be used for backfilling mine workings or for reclamation and rehabilitation of mined areas (Lottermoser, 2010). Thus, if re-use or recycling of processing mine wastes is planned, then a thorough understanding of the geochemical and mineralogical transformation of the particular waste needs to be established prior to its application.

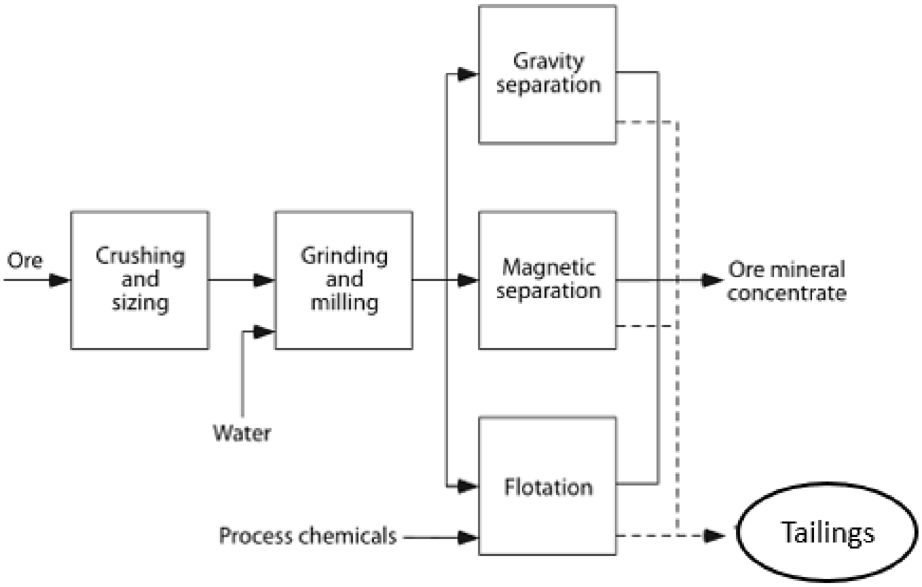


Fig.2.2: Illustration of ore beneficiation or mineral processing operation, whereby the mined ore is processed to yield processing mine waste and ore mineral concentrate (after Ripley *et al*., 1996).

2.3.3. Metallurgical mine waste

The processing of metal ore produces a mineral concentrate which is an input to extractive metallurgy (Lottermoser, 2010). According to Ripley *et al*., (1996) extractive metallurgy is largely based on hydrometallurgy (involves the use of solvents to dissolve the element of interests) and pyro-metallurgy (involves the use of heat to breakdown the crystal structure of the ore mineral), and to a lesser degree, on electrometallurgy which uses electricity. These metallurgical methods destroy the chemical structure of elements and results in the production of various metallurgical mine wastes including atmospheric emissions, flu dusts, slag, leached ore and wastewater (Fig. 2.3).

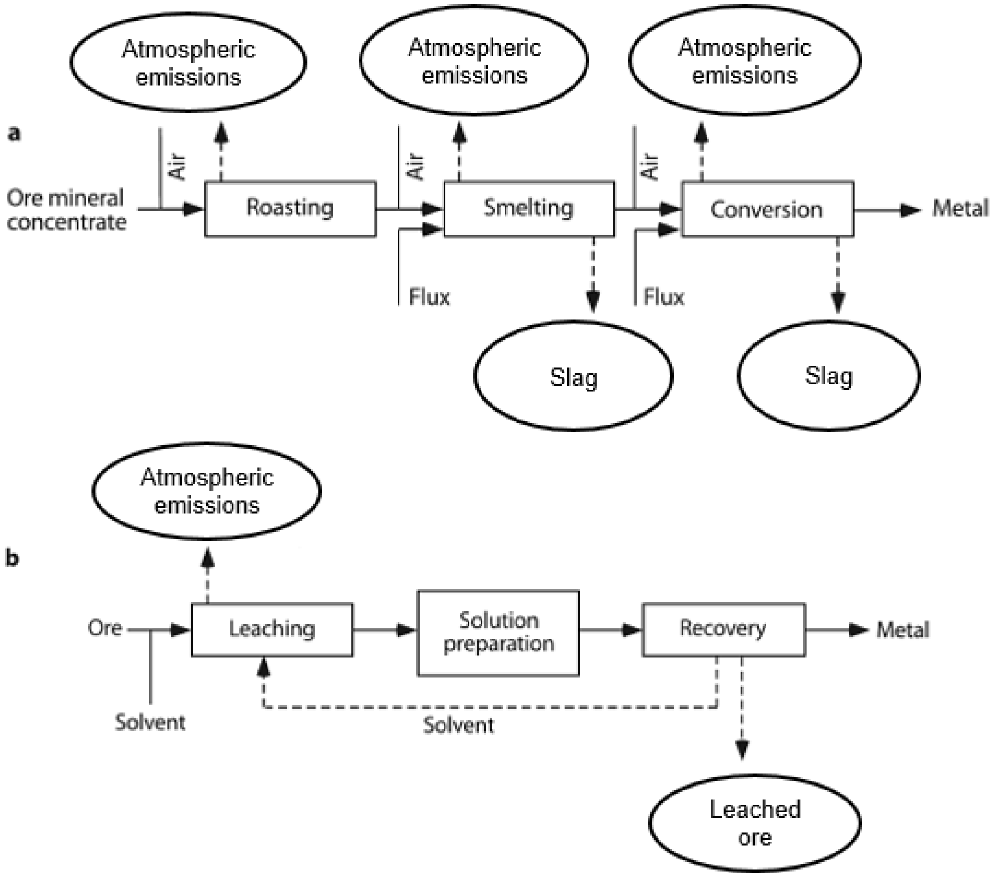


Fig.2.3: Illustration of (a) pyro-metallurgical and (b) hydro-metallurgical operations, whereby the mined ore is treated to yield metal and metallurgical mine waste (Lottermoser, 2010).

In general, mining, mineral processing, and metallurgical operation results not only in the production of commercial metals, but also in the production of immense quantities of mine wastes (Fig. 2.2 and 2.3). However, mine wastes have been reported to commonly contain hazardous dusts, radioactive particles, and low commercial value toxic metals and metalloids at elevated concentrations, organic and inorganic additives from treated ore, processed chemicals, and leachates from the treated ore (Blowes *et al.* 1995). Consequently, the discharge of mine wastes into landfill without safe management or lack of monitoring by mine operators could cause environmental pollution and other prolonged adverse environmental impacts thereby affecting the entire ecosystem (Joeng, 2003).

According to Godfrey *et al*. (2007) in South Africa mining activities in the Witwatersrand areas has led to the generations of millions of tons of mineral waste from the treatment of 4000 million tons of ore. Lottermoser (2010) further reported that over 1100 mines in South Africa; contribute to 73.2 % of the country's total solid waste stream, with approximately 25,000 ha of land utilized as dumping areas in the form of tailings storage facilities. Consequently, mine wastes represent the greatest proportion of waste produced by industrial activity. However, this is mainly because metal ores of increasingly lower grades are being exploited, and more wastes are being produced as a result.

Mine waste production is not a single nation's challenge but a global one. According to BRGM (2001), more than 4,700 million tons of mine wastes are stored all over the European Union (EU). Furthermore, in China over 2688 collectively state-owned and individually owned metal mines account for 70 % of the total solid waste. Each year, these mine wastes occupy an additional 2000 hectares (ha) of land. The production of mine waste is particularly significant throughout the world.

However, mine wastes generated at different mines vary considerably in their properties depending on the mined ore and implemented mining and mineral processing techniques (Lottermoser, 2010). As such, to alleviate mine wastes challenges, every mine waste will require its own waste characterization, prediction, monitoring, control and treatment. Moreover, regulations should be enforced to ensure that the environmental performance of mining companies is adequate in order to continue to improve its environmental operation and operate in a sustainable manner.

2.3.4. Tailings mine waste

Tailings are finely ground residual mine waste from ore beneficiation or mineral processing operation, mainly deposited into an impoundment or tailing storage facility as a slurry (Blowes *et al*. 1995). Although, the grain size of tailings depends on the nature of the ore and the milling process, tailings typically range in size from fine sand to silt grain size (Lottermoser, 2010). In general, tailings dumps contain a range of unwanted inorganic potentially toxic metals and metalloids which are primarily bounded to a variety of gangue minerals present within the tailings (i.e., sulphide, carbonate, oxide and silicate minerals), processed chemicals (reagents such as cyanide and sulfuric acids), organics and leachate effluents from the treated ore (Lottermoser, 2010).

Consequently, the physicochemical characteristics of the tailings vary considerably, depending on the mineralogy and geochemistry of the treated ore, added chemical reagents during processing, and mineral processing or ore treatment techniques (Lottermoser, 2010). There are around 400 tailings in the country, some of which are the largest in the world (Ulrich and Fourier, 2003). According to AngloGold Ashanti (2004), most of the tailings dams are found in the Witwatersrand basin.

However, according to Romero *et al*. (2007), lack of control or safe management of large volumes of tailings dumps after mine closure or when the mine is abandoned, could consequently contribute to the environmental pollution through various ways such as, contamination of streams and rivers by acidic leachate effluent, contamination of streams due to surface run-off from the impoundment area, air and water contamination due to wind erosion of dried-out tailings, physical and aesthetic modification to the environment and difficulty to establish vegetation cover to permanently stabilize tailings due to unfavorable soil conditions (Oelofse *et al*. 2007).

2.4. Physical and chemical characteristics of tailings dumps

The physical and chemical characteristics of tailings dumps vary considerably, depending on the type of ore mined, added chemical reagents during processing, and mineral processing or ore treatment techniques (Lottermoser, 2010). However, the physical and chemical characteristics of tailings govern the actual release or leaching of potentially toxic metal and metalloids species from tailings to the environment (Hiller *et al*. 2013).

2.4.1. Physical characteristics of tailings dumps

The physical characteristics of tailings dumps involve bulk density, particle size distribution, air-filled porosity, and moisture content (Moncur *et al*. 2005). However, there is a great relationship amongst these parameters, as they control the actual release or transport of potentially toxic metal and metalloids species from the tailings to receiving aquatic systems (van der Sloot and Dijkstra, 2004; Hiller *et al*. 2013). Although, the grain size of the tailings depends on the nature of the ore, and the milling process, tailings typically range in size from fine sand to silt grain size (Blowes *et al*. 1995). Nevertheless, according to Blowes *et al*. (1997) fine grain size of tailings results in high moisture content retained by tailings. Consequently, high residual moisture content of tailings results in a low gas or air-filled porosity, and creates a large surface area for oxidation process at shallow zones of the tailings due to the presence of oxygen and pore waters impeded from the transport and diffusion into deeper un-oxidized zones of the tailings (Sracek *et al*. 2010).

Sracek *et al.* (2010) further reported that a decrease in the porosity of tailings results in compaction, and consequently high bulk density of the tailings. Nevertheless, McGregor and Blowes (2002) attributed the increase in bulk density of the tailings, to the formation of cement layers or hardpans in the unsaturated zone of the abandoned Cu and Co mine tailings at the Zambian Copperbelt in the north of Zambia. Sracek *et al*. (2010) corroborated, and further reported that hardpan or cement layers are very important in; (a) The mitigation of acidic leachate effluent from tailings, because they limit the penetration of oxygen to un-oxidized sulfide minerals in the deeper zones, and (b) They incorporate large quantities of soluble metal species adsorbed or co-precipitated with secondary hardpan minerals such as jarosite and gypsum.

2.4.2. Chemical characteristics of tailings dumps

It is essential to understand the parameters governing the mobility, bioavailability, and eco-toxicity of potentially toxic elements within the tailings and tailings-soil interface. The chemical characteristic of tailings dumps entail the total element concentrations, pH and Eh of the tailings, primary and secondary mineral phases (Sracek *et al*., 2010; Hiller *et al*., 2013). These parameters not only govern the actual release of potentially toxic elements from tailings to the environment, but they also provide crucial information on the present environmental condition of the tailings dumps under evaluation (Hiller *et al*. 2013). The principal environmental concerns associated with tailings dumps results from the oxidation of sulfide minerals (mainly pyrite), and the subsequent release and transport of oxidation products (Blowes *et al.* 1995). The oxidation of sulfides may result in the formation of leachate effluent with low pH laden with high concentrations of sulfates and potentially toxic metal and metalloids species (Blowes *et al*. 2003). Nevertheless, according to the work done by Hiller *et al*. (2013), under low pH or acidic conditions many metals and metalloids species such as Cu, Fe, Pb and Zn, are generally more soluble and mobile than in near-neutral pH conditions. Although, according to Conesa *et al*. (2008) metalloids species such as Ag and Sb may still exhibit mobility in near-neutral pH conditions of the tailings. Romero *et al*. (2007) reported that the net amount of acid generated by sulfide oxidation depends largely on the mineralogical composition of the tailings dumps (Romero *et al*. 2007).

The predominance of carbonates (calcite, dolomite, siderite, and ankerite) and alumino-silicates (feldspar, biotite, muscovite and albite) neutralizes the acidity that might be generated by the oxidation of sulfide minerals, thus generating low pH conditions in the tailings pore water (Romero *et al*. 2007) . Neutralization of the acidity occurs through the dissolution of acid neutralizing minerals such as carbonates and alumino-silicate minerals, as they consume the hydrogen ions (H^+) and generate neutral pH conditions within the tailings pore waters (Lin, 1997; Romero *et al*. 2007; Hiller *et al*. 2013). Consequently, the concentration of dissolved potentially toxic metal and metalloids species in the tailings leachates and pore-waters become relatively low.

However, many researchers lamented the formation of secondary mineral phases such as Fe (lll) or Al (lll) oxides, oxyhydroxides, and oxyhydroxysulphates, from primary oxidation and hydrolysis or dissolution reaction products, as the dominant solid phases that control the chemical element composition, mobility, bioavailability and eco-toxicity of potentially toxic metal species from the tailings to adjacent environments (Lin *et al*. 1997; McGregor and Blowes, 2002; Sracek *et al*. 2010; Hiller *et al*. 2013). To enhance a better understanding of the physicochemical characteristics of tailings it is also essential to understand the origin and mode of occurrence of the potentially toxic elements or heavy metals and the natural attenuation dynamics or geochemical process occurring within the tailings dumps (Hiller *et al*. 2013). This information is crucial when predicting the long-term behavior of tailings material and their environmental remediation strategies.

2.5. Natural attenuation of potentially toxic or heavy metal and metalloids species in tailings dumps

Previous work done by Lin (1997) and Romero *et al*. (2007) on impact of abandoned mine tailings to the adjacent environment reported that the concentration and mobility of dissolved constituents within the tailings are controlled by a complex series of oxidation-neutralization processes, mineral precipitation-dissolution processes, and sorption-desorption processes. Hiller *et al*. (2007) corroborated on neutral low-sulfide/high carbonate tailings impoundment at eastern Slovakia, and further reported that the concentration and mobility of each dissolved constituent i.e. potentially toxic metal and metalloids species in solution, is however a function of pH and mineralogy of the tailings dump.

2.5.1. Oxidation-neutralization processes

The principal environmental concern associated with tailings dumps results from the oxidation of sulfide minerals (mainly pyrite), and the subsequent release and transport of oxidation products (Romero *et al*. 2007). Sulphide oxidation has been extensively studied throughout the world, and is reported that it may result in the formation of acidic leachate effluent with low pH, high concentration of sulfates, and potentially toxic metal and metalloids species (Lin, 1997; McGregor and Blowes, 2002; Romero *et al*., 2007; Hiller *et al*. 2013). According to these authors, the oxidation of sulphide minerals typically pyrite (most common and abundant sulphide mineral in the earth's crust) and the generation of acidic leachate effluent, may be considered to take place in three major steps i.e. pyrite oxidation (oxygen path, chemical reaction 1), ferrous iron oxidation (chemical reaction 2) and ferric iron path (chemical reaction 3).

$$FeS_2\ (s) + 7/2O_2\ (g) + H_2O\ (l) \rightarrow Fe^{2+}\ (aq) + 2SO_4^{2-}\ (aq) + 2H^+\ (aq) \qquad \text{(Eq.1)}$$

This reaction consumes pyrite, oxygen, and water, and releases ferrous iron (Fe^{2+}), sulfates (SO_4^{2-}) and hydrogen ions (H^+) to the tailings pore water, and generates low pH acidic conditions within the tailings. However, according to Sracek *et al*., (2010) in the unsaturated zone of mine tailings, the released ferrous iron (Fe^{2+}) by sulfide oxidation is subsequently oxidized by oxygen to produce ferric iron (Fe^{3+}) and consumes the acidity in the process (Eq. 2), and under high pH conditions there is precipitation of ferric hydroxide (Eq. 3).

$$4Fe^{2+}\ (aq) + O_2\ (g) + 4H^{+}\ (aq) \leftrightarrow 4Fe^{3+}\ (aq) + 2H_2O\ (l) \qquad \text{(Eq.2)}$$

$$Fe^{3+}\ (aq) + 3H_2O\ (l) \leftrightarrow Fe\ (OH)_3\ (s) + 3\ H^{+} \qquad \text{(Eq.3)}$$

Chemical reaction (3) generates acidity in the form of hydronium ion (H_3O^{+}) in solution, and the produced ferric hydroxide can include a variety of secondary Fe^{3+} oxide, oxyhydroxide or oxyhydroxide-sulphate minerals such as goethite, ferrihydrite and jarosite (Dold, 2005). Hiller *et al*. (2013) further reported that these secondary mineral phases or precipitates have the potential to retain relatively high amounts of dissolved concentrations of potentially toxic metal and metalloids species such as Cu, As, Zn, Pb, Ag, Co, Cd, Ni, and Cr, thereby moderating the severity of their environmental effects from the tailings.

Alternatively, Dold (2005) reported that under very low pH conditions (pH<3), the solid ferric (Fe^{3+}) oxyhydroxide or oxyhydroxide-sulphate is unstable and Fe (III) can remain in solution, and oxidize additional pyrite or other remaining sulphide minerals within the tailings as represented by chemical reaction (4):

$$FeS_2\ (s) + 14Fe^{3+}\ (aq) + 8H_2O\ (l) \rightarrow 15Fe^{2+}\ (aq) + 2SO_4^{2-}\ (aq) + 16H^{+}\ (aq) \qquad \text{(Eq.4)}$$

However, any of these chemical reactions can occur spontaneously or can be catalysed by microorganisms such as *Thiobacillus ferrooxidans* that derive energy for metabolism from the oxidation reaction (MMSD, 2001).

In general, according to Dold (2005) the rate of oxidation of pyrite increases with the concentration of ferric iron, thus controlled by the rate of oxidation of ferrous iron, and decreases with the concentration of ferrous (Fe^{2+}) and hydrogen (H^{+}) ions. Oxidation reaction equation (4) occurs at low pH conditions. Moncur *et al*., (2005) reported that under low pH conditions, ferrous iron (Fe^{2+}) becomes the dominant form of ferric iron (Fe^{3+}) in solution. Furthermore, for every mole of pyrite (FeS_2) oxidized by ferric iron (Fe^{3+}) 16 moles of hydrogen ions (H^{+}) is generated (chemical reaction 4).

Nevertheless, the net effect of these oxidation reactions is to release hydrogen ions (H^+), which lowers the pH and maintains the solubility of ferric iron (Fe^{3+}). Aqueous ferric iron (Fe^{3+}) is a very aggressive oxidant, and when it reacts with sulphide minerals it significantly generates greater quantities of acid than are generated by oxygen path oxidation (Eq.1 and 4). However, according to Dold (2005) the oxidation of other sulphide minerals such as sphalerite [Zn, Fe(S)] and chalcopyrite ($CuFeS_2$) can occur or may occur within tailings (Eq. 5 and 6), although may not necessarily generate acidity, but releases significant amounts of soluble potentially toxic metal and metalloids cations such as Fe^{2+}, Zn^{2+} and Cu^{2+}, respectively to the tailings pore solution.

$$ZnS\ (s) + 2\ O_2 \rightarrow Zn^{2+} + SO_4^{2-} \qquad \text{(Eq.5)}$$

$$CuFeS_2\ (s) + 4\ O_2 \rightarrow Fe^{2+} + Cu^{2+} + 2\ SO_4^{2-} \qquad \text{(Eq.6)}$$

Oxidation mechanism or processes control the solubility, and therefore concentration and mobility of dissolved potentially toxic metal and metalloids species by lowering of the pH conditions of the tailings pore solution (Romero *et al*. 2007). The solubility of potentially toxic metal and metalloids species increases with decreasing pH, and more dissolved metals become mobile and bioavailable to the receiving surface and groundwater systems (Hiller *et al*. 2013).

However, the persistence of sulphide oxidation is mainly attributed to the absence of the most effective gangue minerals incorporated in the tailings, which can neutralize the acidity generated by sulphide oxidation process (Moncur *et al*. 2005). These minerals are mainly carbonates (calcite, dolomite, ankerite, and siderite) and alumino-silicates (plagioclase, feldspars, biotite, and muscovite, and chlorite), which buffer the pH, thereby attenuating the acidity generated by sulphide oxidation (Moncur *et al*. 2005). Neutralization of the acidity in the tailings occurs through the dissolution of carbonates and aluminium-silicate minerals, which consumes the hydrogen ions (H^+) and generates neutral pH conditions within the tailings. Consequently, the concentrations of dissolved toxic metal and metalloids species in tailings leachates and pore water solution become relatively low (Hiller *et al*., 2013).

Nevertheless, according to Lapakko (2002), the dissolution of carbonate and alumino-silicate minerals releases alkali earth and metal cations, including Ca^{2+}, Mg^{2+}, Fe^{2+}, and Mn^{2+}, which may precipitate and results in the formation of secondary mineral phases. For example, the dissolution of calcite can be described as follows:

$$CaCO_3\ (s) + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad (Eq.7)$$

This chemical reaction describes the dissolution of calcite which consumes hydrogen ions (H^+) generated by sulphide oxidation, and releases calcium cation (Ca^{2+}) to the tailings pore water solution. Consequently, this process generates neutral to alkaline pH conditions. Sracek *et al*. (2010) substantiate by indicating that when fast-acting neutralization minerals like calcite are present in the solid phase, they neutralize acidity produced by the oxidation of pyrite, and gypsum precipitates simultaneously (chemical reaction 8),

$$CaCO_3\ (s) + 2H^+ + SO_4^{2-} + H_2O \rightarrow CaSO_4.2H_2O\ (s) + H_2CO_3 \qquad (Eq.8)$$

However, gypsum dissolves later as the carbonate content of the tailings dissolves, and the pH is buffered to near neutral (Sracek *et al*. 2010). Lapakko (2002) further reported that the carbonate minerals reactivity decreases from calcite, siderite, dolomite, and magnesite.

Nevertheless, according Blowes *et al*. (2003), when reactive carbonates are depleted or absent, alumino-silicate minerals such as chlorite, biotite, feldspar, muscovite, and albite in the tailings, play a role in the long-term acid neutralization. Although, according to Dold (2005), most silicate minerals provide much less neutralizing capacity than carbonates because of their slow reaction kinetics. The dissolution of alumino-silicates such as biotite can be described as follows:

$$K\ (Mg\ Fe)_{1.5}\ AlSi_3O_{10}\ (OH)_2 + 10\ H^+ \leftrightarrow K^+ + 1.5\ Mg^{2+} + 1.5\ Fe^{2+} + Al^{3+} + 3\ H_4SiO_4 \qquad (Eq.9)$$

The dissolution of alumino-silicates consumes the acidity (H^+), but also contribute to the release of base cations (Ca^{2+}, Mg^{2+} and Fe^{2+}), alkali metals (Na, K) and dissolved Si and Al to the tailings pore water (Blowes *et al*. 2003). Moreover, Dold (2005) reported that the attenuation of Al (III) and K^+ ions released by the dissolution of alumino-silicates can also occur through further reactions to form secondary minerals such as aluminium oxide, hydroxide and hydroxysulphates, as describe by chemical reaction (10):

$$2\ Al^{3+} + 2\ H_4SiO_4 + H_2O \leftrightarrow Al_2Si_2O_5\ (OH)_4 + 6\ H^+ \qquad \text{(Eq.10)}$$

As such, sulphide oxidation and neutralization reaction mechanisms or processes have a great influence on the mobility of potentially toxic metal and metalloids species in the tailings, and their retention to primary and secondary phases within tailings. It is therefore necessary to evaluate the geochemical and mineralogical transformation in tailings material, as this will provide significant information to better understand toxic metal species mobility and attenuation dynamics within the tailings, and their potential environmental impacts.

2.5.2. Precipitation-dissolution processes

According to the work done by Dold (2005), the formation of secondary ferric (Fe^{3+}) or aluminium (Al^{3+}) oxide, hydroxide, hydroxysulphate minerals results in the attenuation of trace metals released through primary oxidation and hydrolysis or dissolution reaction products. Hiller *et al*. (2013) corroborated by further reporting that the precipitation of secondary minerals under certain geochemical conditions, play an important role on the mobility and attenuation of trace metals, and thereby controlling the concentration of dissolved trace metals through adsorption and co-precipitation onto the mineral surfaces.

The most abundant dissolved constituents derived from sulphide oxidation and acid neutralization reactions are SO_4^{2-}, Fe (ll), Fe (lll), HCO_3^- and the major cations Ca^{2+}, Mg^{2+}, Na^+, K^+, and Al (lll) ions (Blowes *et al*. 2003). These dissolved constituents react in effluent waters, resulting in the precipitation of a number of precipitates including gypsum ($CaSO_4.2H_2O$), jarosite [$KFe_3\ (SO_4)_3(OH)_6$], goethite (FeOOH), ferrihydrite [$Fe_8\ (OH)_9$], and kaolinite [$Al_2Si_2O_5\ (OH)_4$], depending on the pH-Eh conditions (Blowes *et al*. 2003). Work done by Romero *et al*. (2007) and Sracek *et al*. (2010) indicates that the precipitation and dissolution of these mineral phases limits the concentration of dissolved metal and metalloids species in pore water, through sorption process onto the mineral surfaces and provides substrates for the attenuation of dissolved metal and metalloids species.

The formation of secondary Fe (III) oxyhydroxides has been observed to retain relatively high concentrations of dissolved Cu, Hg, As and Sb in the tailings impoundment at Markušovce, eastern Slovakia (Hiller *et al*. 2013). Romero *et al*. (2007) made similar observations within the 'El Fraile' tailings in Taxco, central-southern Mexico, where the precipitation of Fe (III) oxyhydroxides as goethite, strongly trap high concentration of dissolved Cu, As, Zn, and Cd through adsorption and co-precipitation within the active oxidation zone of the tailings impoundment. Hiller *et al*. (2013) also reported that the formation of secondary covellite (CuS) on the surfaces of sphalerite [(Zn, FeS)] has also been observed to limit dissolved copper concentrations (Fig. 2.4).

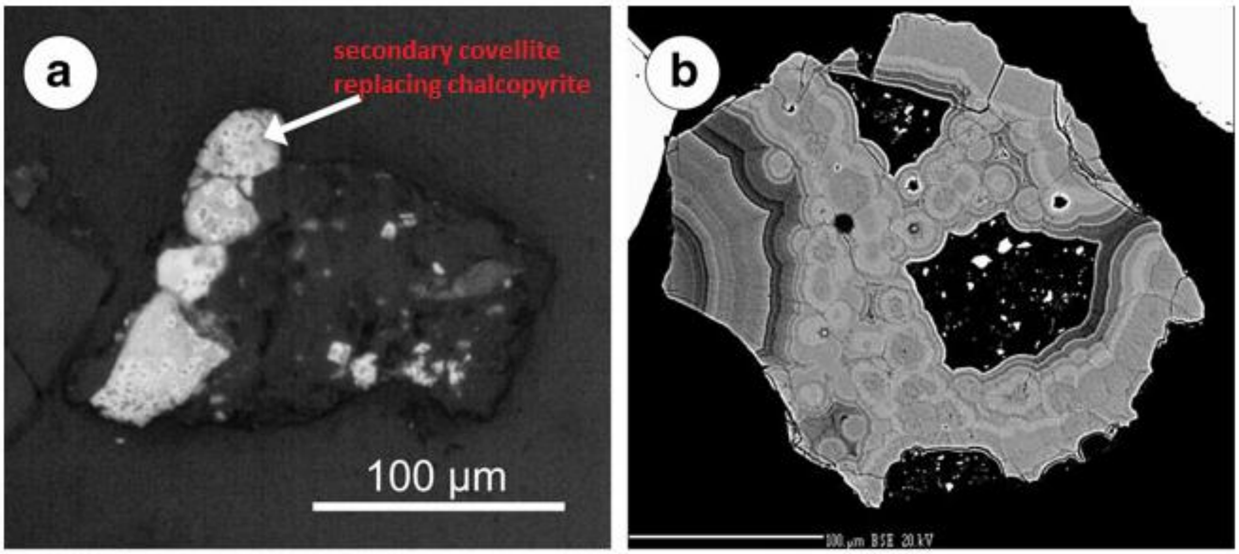


Fig. 2.4: Microscopic photograph in reflected polarized light showing; (a) Replacement of chalcopyrite grain by the precipitation of secondary covellite, and (b) Precipitation of secondary Fe oxyhydroxide phase (light gray coatings) filling cracks in a carbonate grain (dark gray) (adopted from Hiller *et al*. 2013).

However, according to Murad and Rojik (2003), the extent of formation of secondary precipitates in tailings is dependent on the pH-Eh conditions and the availability of primary oxidation and hydrolysis or dissolution reaction products such as, Fe (III), SO_4^{2-}, Al, Ca, Na, H_3O^+ and K^+. Murad and Rojik (2003) further reported that precipitation of secondary minerals can occur in near neutral or even in alkaline environments provided the acid generated by the oxidation of sulphide minerals is significantly neutralised. Romero *et al*.

(2007) corroborates by indicating that highly water-soluble sulphates such as gypsum ($CaSO_4$. $5H_2O$) are formed under oxidizing conditions and high evaporation rates, and can store acid and metals which can be released by the dissolution of soluble gypsum.

Sracek *et al*. (2010) reported that the stability of gypsum requires the presence of calcium in tailings pore water, which is provided by the dissolution of carbonates like calcite. However, McGregor and Blowes (2002) indicated that with time, gypsum dissolves and release acid and metals to the tailings pore water through desorption process by transformation to jarosite [K, Na, H^3O^+, Fe (lll) hydroxysulphate]. McGregor and Blowes (2002) further reported that jarosite is stable in saturated conditions, but becomes unstable due to changes in the geochemical conditions within the tailings or changes in the degree of saturation, thus it may undergo replacement by goethite as described by chemical reaction (11).

$$KFe_3 (SO_4)_2 (OH)_6 \leftrightarrow K^+ + 2\ SO_4^{2-} + 3FeOOH + 3H^+ \qquad \text{(Eq.11)}$$

The transformation of jarosite to goethite secondary precipitates decreases the surface area available for adsorption of potentially toxic metal and metalloids species, and consequently, this may cause the release of acid, and previously adsorbed and co-precipitated metals including Fe^{3+} ions to the tailings pore water which may further encourage sulphide oxidation process (Sracek *et al*. 2010). Nevertheless, depending on geochemical conditions such as pH-Eh and degree of saturation, the formation of these secondary minerals plays an important role in the transport and attenuation of trace metals, controlling both the solubility and concentrations of dissolved metal and metalloids species, through adsorption and co-precipitation, thereby retaining oxidation products before percolating water reaches the receiving groundwater and surface waters (McGregor and Blowes, 2002; Dold, 2005; Romero *et al.*, 2005; Sracek *et al*. 2010).

2.5.3. Sorption-desorption processes

Sorption-desorption processes are key geochemical processes or natural attenuation dynamics which govern the actual mobilization, and potential release of potentially toxic metal and metalloids species from tailings to adjacent aquatic systems (Hiller *et al*. 2013). Nevertheless, metals and metalloids species may be present in solution either as positively or negatively charged and in different redox states (Violante and Pigna, 2008). Violante and Pigna (2008) further reported that metals and metalloids species occur predominantly in cationic form (Cu, Pb, Zn, Co, and Ni), while other metal and metalloids species are present in anionic form (As, Mo, B, and Se).

However, sorption and desorption of metals and metalloids species vary greatly in cationic and anionic forms, as cations such as Cu, Pb, Ca, Mg, Cr, Ni, Co, Zn, Al, Mn, and Fe are often strongly sorbed onto the mineral surfaces of the present inorganic sorbents like secondary mineral phases such as amorphous Fe (lll) or Al (lll) oxyhydroxides or hydroxysulphate (Violente *et al*. 2002; Hiller *et al*. 2013). Work done by Kabata-Pendias, (2001) indicated that sorption-desorption processes may be affected by many factors, amongst which are pH, nature of the sorbents, redox reactions and the presence of carbonates in solution.

Furthermore, Sparks (2003) corroborates by reporting that under high pH conditions sorption decreases as many metal and metalloids cations become less soluble and mobile. These conditions are associated with the presence of effective carbonate minerals, as their dissolution neutralizes the acidity thereby generating high pH conditions (Sparks, 2003). Changes in geochemical conditions (pH and Eh) results in the precipitation and dissolution of secondary mineral phases such as gypsum, Fe (lll) or Al (lll) oxides and hydroxysulphates, which in turn, permanently or temporarily sequester potentially toxic metal and metalloids species through sorption process (Hiller *et al*. 2013).

As such, complex geochemical processes or natural attenuation dynamics including oxidation-neutralization processes, precipitation-dissolution processes and sorption-desorption processes which occur within the tailings dumps, must therefore be well studied to understand toxic metal and metalloids species mobility, bioavailability, and eco-toxicity, and to predict the possible environmental impacts which may be induced by the leaching of potentially toxic metal species from the tailings dumps.

2.6. Metal speciation and sequential extraction scheme

Most studies dealing with particulate metals and metalloids species associated with the mine waste, suspended matter or bottom sediments in natural water systems concern the measurement of the total concentration of metal (Moncur *et al*. 2005; Romero *et al.* 2007; Hiller *et al*. 2013). Relatively few attempts have been made to evaluate the geochemical partitioning of metals and metalloids species among the various forms in which they might exist in the solid waste (Okoro *et al*. 2012; Arenas-Lago *et al*. 2014). The measurement of the total concentration of metal and metalloids species as criteria to assess waste contamination provide inadequate information pertaining to their mobility and bioavailability, since not all forms of a given metal and metalloid species are equally soluble in a solid waste (Tessier *et al*. 1979; Li and Thornton, 2001). However, total concentration of metal and metalloids species do place an upper limit on metal and metalloid species bioavailability. Thus, to estimate the real mobility, bioavailability, and potential toxicity of metals and metalloids species, it is important not only to determine their total concentration but also the different chemical forms or ways of binding between major and trace metals and the solid phases of the sample (Joeng, 2003).

Elements are present in the soil or solid waste in different fractions like sulphides, sulphates, carbonates, silicates, oxides and also as native elements in minerals, which may strongly affect the way the element behaves in the soil or solid waste, depending on its mobility, bioavailability, toxicity and chemical interactions within the soil or waste (Arenas-Lago *et al*. 2014). Nevertheless, for the present study, using fractionation methods based on sequential extractions, we need to know how the potentially toxic metal and metalloids species are distributed in the tailings and tailings soil-interface in order to study their bioavailability and possible toxicity on the environment as pertains to surface and groundwater systems. However, according to Joeng (2003) metal speciation has been extensively studied using selective chemical extraction methods and sequential extraction techniques. Sequential extraction techniques are recently widely employed to obtain information on metal speciation in soils, sediments and solid waste, and are based on a combination of specific extractions (Tessier *et al*. 1979). Although the use of sequential extraction scheme is time consuming, but furnishes detailed information about the origin, mode of occurrence, biological and physiochemical availability, mobilization and transport of trace metals and metalloids species (Joeng, 2003). Nevertheless, different sequential extraction procedures have widely been used to study the binding forms of metals and metalloids speciation in solid waste, soil, and sediments (Tessier *et* *al*. 1979; Usero *et al.* 1998). However, most of them mimic the basic procedure initially developed for sediments by Tessier *et al*. (1979) for the partitioning of particulate trace metals and metalloids into five fractions; exchangeable fraction, bound to carbonate fraction, bound to oxide fraction, bound to sulphides and organic matter fraction and the silicate or residual fraction. The BCR (Community Bureau of Reference) also mimic the basic procedure initially produced by Tessier *et al*. (1979) with the main difference in the first fraction of the procedure, whereby the exchangeable and carbonate bound fractions are combined instead of extracting them separately (Ure *et al*. 1993).

Generally, in a sequential extraction scheme a known mass of a solid waste sample is subjected to a series of reagents or extractants, to selectively dissolve a mineralogical constituent, which is a potential carrier of trace and minor metals in a sample, with the basic assumption that the reagents are able to dissolve one phase selectively without the solubilization of others (Fonseca and da Silva, 1998). The reagents or extractants commonly used in sequential extraction fall within the groups of un-buffered salts, weak and strong acids, reducing and oxidizing agents (Joeng, 2003).

2.7. Overview of sequential extraction fractions, reagents

Different sequential extraction procedures have widely been used to study the binding forms of metals and metalloids speciation in solid waste, soil and sediments (Tessier *et al*. 1979; Usero *et al.* 1998). However, most of them modify the basic procedure initially developed for sediments by Tessier *et al*. (1979) for the partitioning of particulate trace metals and metalloids into five fractions; exchangeable fraction, bound to carbonate fraction, bound to oxide fraction, bound to sulphides and organic matter fraction and the silicate or residual fraction. According to Joeng (2003) sequential extraction procedures are operationally defined, as such the efficiency of each extraction is dependent on factors such as chemical reagents employed, extraction time, and solution/solid ratio. The following paragraphs describe the application of the most widely used reagents or extractants for the extraction of each fraction and their limitations or drawbacks.

2.7.1. Exchangeable fraction

The exchangeable fractions include weakly adsorbed metals (K, Ca, and Mg) which exhibit high mobility under acidic conditions and readily bioavailable to the environment (Tessier *et al.* 1979). Tessier *et al*. (1979) further reported that high mobility of metals in this fraction is pH dependent, and metals are retained on the solid surface by relatively weak electrostatic interaction. Moreover, Okoro *et al*. (2012) corroborated that metals in this fraction can be easily released by ion exchange processes, and can also be co-precipitated with carbonates present in the solid waste.

However, the most widely used chemical reagents for leaching the metals bound to the exchangeable fraction can be classified as acetate and chlorite salts, ammonium salts and nitrate salts (Filgueiras *et al*. 2002). Acetate (NH_4OAc) and chlorite ($MgCl_2$) salts at 1 M concentration have been the most extensively used reagents (Tessier *et al*. 1979). Nevertheless, in the present study sodium acetate (NaOAc) at 1 M concentration and pH 8.2 was employed to leach metals bound to the exchangeable fraction. Although, ammonium (NH_4Cl) and nitrates ($NaNO_3$) salts can been used, but they have been reported to lower the pH and encourage the hydrolysis of clays (Filgueiras *et al*. 2002).

2.7.2. Carbonate fraction

Numerous studies have shown that this fraction contain significant concentration of metals which are soluble and readily available (Tessier *et al*. 1979; Kontopoulos *et al*. 1995; Beck *et al*. 2001; Okoro *et al.* 2012). High concentration of Pb, As and Cd, in the carbonate fraction were observed by Kontopoulos *et al*. (1995) within the sulphidic tailings in Lavrion. This fraction has been reported to be susceptible to changes of pH, and the leaching metals is achieved through dissolution of a fraction of the solid material at pH close to 5.0 (Okoro *et al*. 2012). The most widely used chemical reagent for the extraction of trace metals and metalloids associated with the carbonate fraction in soils and sediments is 1M sodium acetate (NaOAc) adjusted to pH 5.0 with acetic acid (HOAc) (Tessier *et al*. 1979). However, similar chemical reagents ware employed in the present study, although the mineralogy of the studied material (tailings) governed the selection of 1M sodium acetate (NaOAc)/acetic acid (HOAc) at pH 5.0.

2.7.3. Reducible or Fe and Mn hydroxide associated fraction

It is well studied that iron and manganese oxides exists as nodules, concretions, cement or coatings between particles (Tessier *et al*. 1979). These oxides have been reported to be excellent scavengers for potentially toxic elements species because of their greater adsorption capacity, and are thermodynamically unstable under anoxic geochemical conditions i.e., they dissolve as the redox potential decreases (at low Eh) and re-precipitate as the geochemical environment becomes oxygenated (Hiller *et al*., 2013). However, the scavenging of potentially toxic elements species by Fe and Mn oxides can occur as a combination of precipitation, adsorption, surface complex formation, and ion exchange (Hall *et al*. 1999).

In principle, the reducible fraction could be split into three fractions; easily reducible fraction (Mn oxides), moderately reducible fraction (amorphous Fe oxides), and poorly reducible fraction (crystalline Fe oxides) (Hall *et al*. 1999). Nevertheless, this classification is addressed in a few schemes, and in the present study this classification was considered for a single extraction, as prescribed by several authors (Tessier *et al*. 1979; Lu *et al*. 2014). Several chemical reagents at 0.25 M concentration of hydroxylamine hydrochloride ($NH_2OH.HCl$) in 0.25 M HCl or in 25 % (v/v) acetic acid (HOAc) have been widely employed for the extraction of metals bound to Fe and Mn oxides (Tessier *et al*. 1979; Chao and Zhou, 1983). Chao and Zhou (1983) compared the efficiency of these chemical reagents to dissolve the amorphous and poorly crystalline iron oxides. They observed that the extraction of these oxides by hydroxylamine hydrochloride (NH2OH.HCl) in 0.25 M HCl depends on acid concentration and the temperature of the reaction. At elevated temperatures, hydroxylamine hydrochloride (NH2OH.HCl) in 0.25 M HCl can attack primary and secondary silicate minerals although managed to dissolve 60 % of the tested minerals, meanwhile at room temperature this reagent seemed to be specific and dissolve 1 to 2% of the minerals tested. However, the extraction of these oxides by 0.25 M concentration of hydroxylamine hydrochloride ($NH_2OH.HCl$) in 25 % (v/v) acetic acid (HOAc) demonstrated that at 70ºC dissolved 1 to 4 % of the crystalline Fe oxides, depending on the reaction time. Chao and Zhou (1983) further indicated that a longer reaction time can overestimate the amorphous Fe oxide fraction. However, they concluded that a better reaction time for the use of hydroxylamine hydrochloride ($NH_2OH.HCl$) in 25 % (v/v) acetic acid (HOAc) as an extractant is 90 min with < 2% of the crystalline Fe oxides dissolved. Nevertheless, in the present study, 1M hydroxylamine hydrochloride ($NH_2OH.HCl$) in 25 % (v/v) acetic acid (HOAc) was used as a chemical reagent for the extraction of Fe and Mn oxide fraction at pH of 2.0 for 96^{o}C. The increase in concentration from 0.25M to 1M hydroxylamine hydrochloride ($NH_2OH.HCl$) in 25 % (v/v) acetic acid (HOAc) has been reported to increase the extractability of metals (Lu *et al*., 2014).

2.7.4. Bound to organic matter and sulphide fraction

Trace metal may be bound to various forms of organic matter such as living organisms, detritus, or coatings on mineral particles, through bioaccumulation or process (Okoro *et al*. 2012). This fraction is considered as the immobile fraction and the extracts obtained from this fraction are metals bound to sulphides under oxidizing conditions. However, according to Filgueiras *et al*. (2002) the organic matter can be degraded under oxidizing conditions leading to the release of soluble trace metals, although the organic fraction released is considered not to be bioavailable since it is thought to be associated with stable humic substances that release small amount of trace metals in a slow manner.

Several chemical reagents have widely been used for the dissolution of sulphide minerals or trace metals bound to the organic fraction, and these include H_2O_2-asorbic acid, oxalic acid, mixture of $KClO_3/HCl$, mixture of $KClO_2/HCl$ followed by 4 M HNO_3 (Tessier *et al*. 1979). However, Chao and Sanzalone (1977) observed that a mixture of $KClO_2/HCl$ followed by 4 M HNO_3 leach was most efficient in dissolving sulphides such as pyrite, galena, cinnabar and chalcopyrite, although there is a probability of causing partial destruction of silicates along the edges and surfaces. As such to overcome this drawback Chao (1984) reported that the H_2O_2-asorbic acid leach will not attack other mineral phases such as silicates. The H_2O_2-asorbic acid leach is also prescribed by Tessier *et al*. (1979).

2.7.5. Residual or silicate fraction

The residual fraction contains mainly primary and secondary minerals which may retain high quantity of trace metals within their crystal structure. This fraction is also considered as the immobile fraction and the trace metals retained are not expected to be released into solution in the long term, however care must be taken since any change in the geochemistry (acidic conditions) may cause them to be displaced to more mobile fractions, thereby increasing their mobility and availability (Arenas-Lago *et al*. 2014). Nevertheless, this fraction is commonly dissolved with highly concentrated acids such as HNO_3, HF, $HClO_4$, HCl and species digestion procedures (Okoro *et al*., 2012). However, in the present study a strong triple acid digestion of HF with HCl/HNO_3 was employed to dissolve the silicate fraction, similarly employed by Tessier *et al*., (1979). Sequential extraction is an operationally defined scheme; as such to attain qualitative results from each extraction care must be taken on selecting an appropriate reagent, extraction time, solution/solid ratio governed by an understanding of the mineralogy of the solid waste (Joeng, 2003).

2.8. Sequential extraction drawback

Sequential extraction is an operationally defined scheme (Dold, 2005), thus for quality assurance the following factors were must be into consideration: (a) selectivity of chemical reagents (care was taken when selecting chemicals reagents since some chemicals have the ability to attack other fractions, (b) extraction time and nature of contact, and solubility of solid compounds (care was taken on extraction time to avoid the solubilization of other phases, particularly the organic matter.

2.9. Tailings leaching and potential environmental impact

Tailings dumps are mineral waste generated from mining activities, and have been reported to represent a potential risk for the environment, mainly aquatic system through the leaching of potentially toxic elements occurring in a variety of minerals present in the tailings (Romero *et al*., 2007; Sracek *et al*., 2010; Hiller *et al*., 2013). Several studies showed that tailings dump usually have high pH and an excess of elements such as Cu, Cd, As, Hg, Sb, Ni, Pb, Zn, and Cr (Sracek *et al*., 2010; Hiller *et al*. 2013). The leaching of these constituents occurs when minerals present within the tailings are exposed to atmospheric oxygen and percolating rainwater. The presence of atmospheric oxygen and infiltrating rainwater, lead to the dissolution and solubilization of minerals present within the tailings, consequently leading to the leaching of potentially toxic elements into the receiving surface and groundwater systems.

It is well documented that the leaching of potentially toxic elements into aquatic ecosystems may contaminate surface and groundwater systems, with the potential to deteriorate water quality and groundwater dynamics in terms of both the quality and quantity of water and its flow direction, increased turbidity on surface waters, rivers, and streams, and the potential loss for aquatic habitat and the establishment of alien invasive species (DMR, 2009; MMSD, 2001). However, the leachability of potentially toxic or heavy metals is affected by their solubility and adsorption capacity, chemistry of extracted pore water, and geochemistry of the tailings (Okoro *et al.,* 2012). Hiller *et al.,* (2013) found that the leachability of Cu, Sb, Hg, and As, is relatively low and the leaching extent is dependent on aqueous chemistry. The geochemistry of the tailings can also influence the constituent released during leaching. Romero *et al*., (2007) reported that the low concentration of dissolved constituents (Zn, As, Cu, Cd, and Pb) within 'El Fraile' a complex series of oxidation, precipitation-dissolution, and sorption-desorption reactions control tailings. This author further reported that the concentrations of each dissolved constituent are a function of pH and mineralogy of the tailings. However, the low concentrations of constituents or potentially toxic elements within the leachate moderate the severity of their environmental impact.

2.10. Beneficial utilization of copper tailings dump in the construction industry

Copper tailings are medium to fine grain sandy material generated from the flotation and concentration stages of copper extraction processes during mining activities, mainly deposited or disposed on landfills as a tailings dump. The copper tailings dump disposal occupies large hectares of land. A good example is the abandoned Musina copper tailings dump which is the current study focus that occupies an estimated surface area of about 4.99 Km^2. Moreover, tailings dump disposal has long been recognized as an environmental problem due to the hazards of earth and aquatic pollution derived from past mining activities (Thomas *et al*., 2013).

According to Onuaguluchi and Eren (2012) the increasing demands for copper and copper allied products have led to the mining and processing of low grade ores with high volume of tailings output. Onuaguluchi and Eren (2012) further reported that for every 1 ton of copper produced; about 196.5 tons of solid and liquid tailings are produced. Lottermoser (2010) corroborated that over 1100 mines in South Africa contribute to 73.2 % of the country's total solid waste stream, with approximately 25,000 hectares of land utilized as dumping areas in the form of tailings storage facilities. Thus, in major copper producing countries like South Africa, Chile, Peru, United States, and Indonesia, large tailings deposits containing billions of tons of copper abound and will inevitably be produced in the incoming years.

Several studies documented the severe environmental impacts induced by copper tailings. Ntengwe and Maseka (2006) observed high concentrations of zinc and nickel in water and sediments soils in streams located near the Chambishi copper mine in Zambia. Singo (2013) observed high concentrations of Pb, Cu, Zn, As and Ni, in soils adjacent to the abandoned copper tailings dumps, in Musina. However, given the menaces associated with copper tailings dump disposal, as part of re-use approach management system it is necessary to plan and establish a potential sustainable beneficial application or utilization of copper tailings dump disposal in the construction industry, in order to mitigate the environmental impacts of copper tailings disposal and the reclamation of previously usurped land. Furthermore, the beneficial utilization of copper tailings dump disposal in the construction industry, will sustain the construction material ensuring employment generation. However, a few studies investigated the utilization of copper tailings dumps disposal in the construction industry, with considerable success. Onuaguluchi and Eren (2012) investigated the properties of copper tailings when used as a potential additive in cement mortar and concrete. They find out that in the case of copper tailing mortars, pre-wetted tailings at 5% addition level reduced the negative effects of dry copper and proved to be the best reuse approach. Nevertheless, in the case of concrete, the copper tailings had a slight negative impact on the slump, porosity and setting time of concrete mixtures, and when compared to the control specimen, they found out that there is improvement in mechanical strength and abrasion resistance.

Marghussian and Maghsoodipoor (1999) investigated the blending of copper tailings with other raw materials in the production of unglazed tiles. These authors observed that tiles containing 40% copper tailings fired at 1025ºC for 1 h presented good mechanical and acid resistance properties. Mahmood and Mulligan (2007) investigated the use of six different mine tailings for unpaved road basement construction. The tailings were tested for the physical characteristics followed by unconfined compressive testing. The results indicated that the tailings sustained more than the minimum amount of stress normally required for filling stopes. Generally, according to Thomas *et al.* (2013) copper tailings has a maximum amount of silica (75%). However, in the present study the copper tailings have a maximum amount of silica (58.28%). In comparison with the chemical composition of natural pozzolanas of ASTM C618-99, the summation of three oxides (silica, alumina and iron oxide) in copper tailings is 90.76%, which exceeds the 70% requirement for class N raw and calcined pozzolans. Thus, copper tailings dump disposal are expected to have good potential to produce high quality pozzolans, thereby sustaining the construction material and industry as such.

CHAPTER THREE

RESEARCH METHODOLGY

This chapter gives an overview of a conceptual framework or experimental protocol and provides insight on the research methodology. The research methodology is divided into field work and the study area, laboratory work, and data analysis or results presentation.

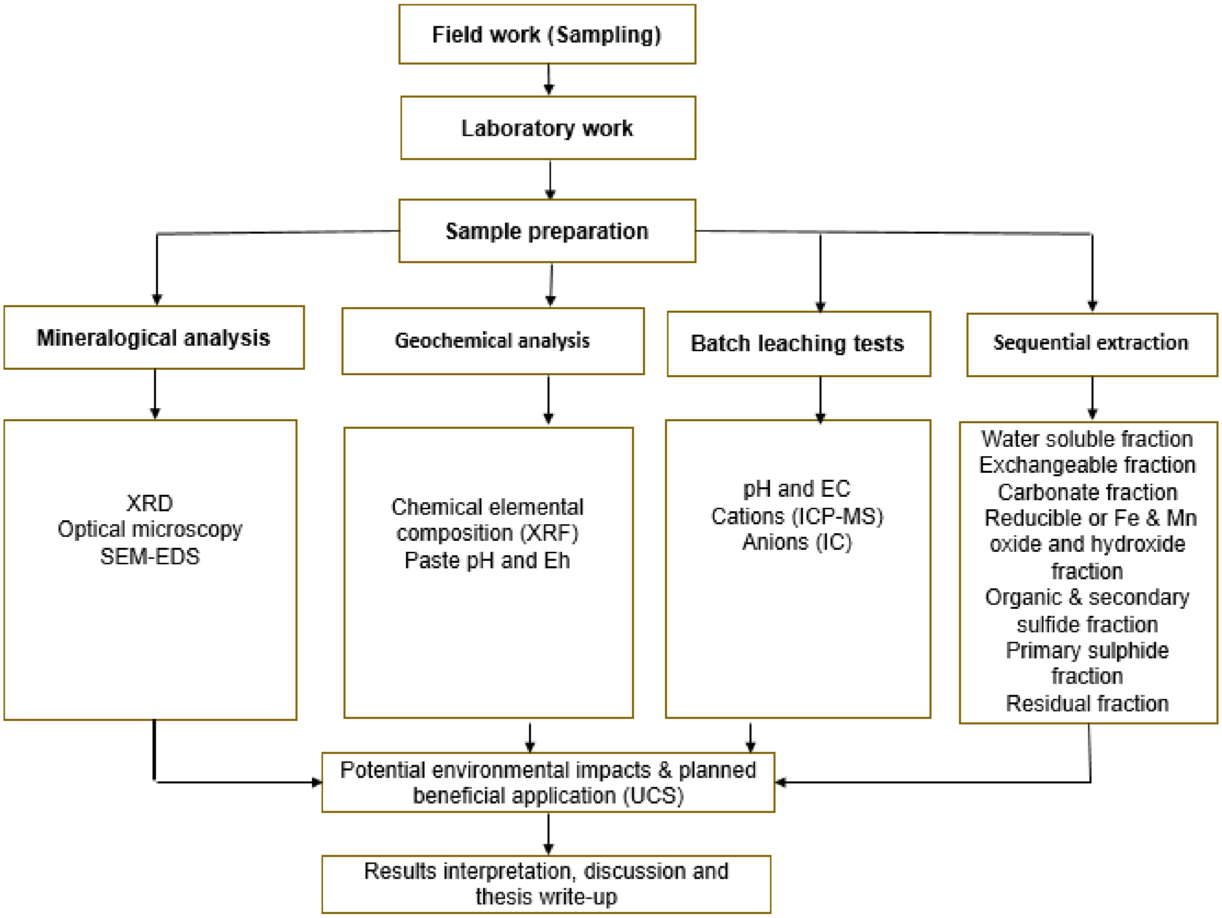


Fig.3.1: Conceptual framework flow-chart or experimental protocol.

3.1. Study area and field work

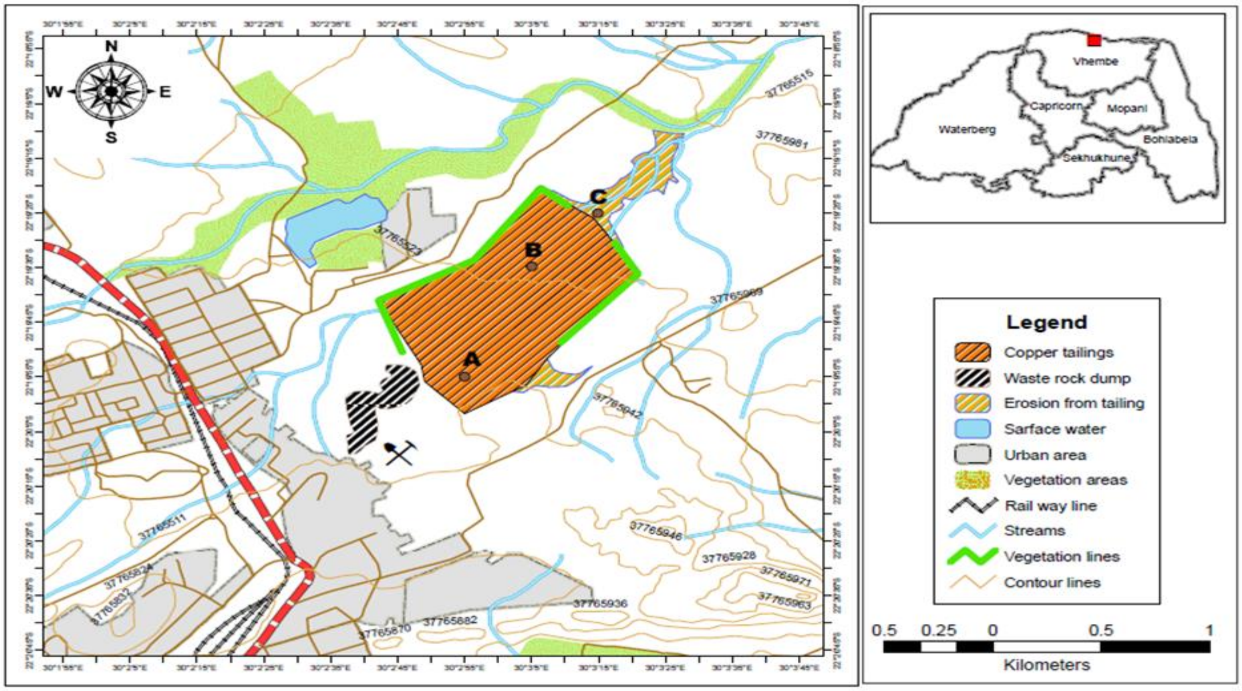


Fig. 3.2: Location of the abandoned copper tailings dump and the selected sampling sites in Musina, Limpopo, South Africa.

The study area is located at Musina (22° 20′ 17″S; 30° 02′ 30″E/22° 33′ 30″S; 30° 04′ 167″E), a small town at the Northern end of Limpopo Province, South Africa. The town of Musina has a long history of mining activities and is a home to several successful mining companies, some of which are abandoned. Nevertheless, some of the exploited mineral resources in the region include iron ore, coal, copper, graphite, magnetite, asbestos, diamonds, and semi-precious stones (Gitari *et al.* 2016). However, copper mining in Musina date back to 1906 when the Musina Development Mining Company started to mine copper ore, and since then over 40 million tons of ore have been mined, recovering about 700,000 tons of copper from chalcopyrite, bornite, and chalcocite (Baele, 1985). The mined ore was processed in an erected concentrator, and copper concentrates were recovered by flotation thickening, and the waste was rejected from the concentrator as tailings dump (Fig. 3.2). Nonetheless, copper mining in Musina stopped in 1992, whereby poor ventilation and water seepage into the mine have also been speculated to force the mine to stop the operation (Cairncross and Dixon, 1995). Thus, the abandoned copper tailings dump disposal in Musina has been exposed to weathering for a period of 25 years (Matshusa and Makgae, 2014). Moreover, geologically, the Musina area is characterized by medium-high grade metamorphic rocks of which the Sand River Gneiss is the oldest (3.7 Ma) and form the basement to a sequence of rock covers of the Beit bridge complex, which according to their dominant lithology are subdivided into the Mount Dowe, Malala Drift and Gumbu Group (Brandl, 1981).

To meet the research aims and specific objectives, three tailings profiles were established, drilled to a depth of 5m (tailings profile A and B) and 3m (tailings profile C) distanced at 1km apart, respectively. Tailings profile A and B were located at the southern-central sector, meanwhile tailings profile C was located at the north-eastern sector of the abandoned copper tailings dump disposal (Fig. 3.2). However, a systematic sampling grid technique was commissioned on the present study by using a square grid and collecting samples from the nodes (interactions of the gridline). At each node, tailings samples were collected at regular depth intervals with the use of a hand drill auger. The sampling sites were selected according to the heterogeneity of the tailings considering color, texture differences, and degree of concretion or contact with the underlying soil or tailings soil-interface. Twelve tailings samples were collected from the established tailings profiles, and preserved in tightly sealed and marked oxygen diffusion-free polyethylene plastic bags to minimize dust contamination, and transported to the laboratory for sample preparation and further analyses.

3.2. Laboratory work

Laboratory work entailed sample preparation to prepare the samples for all subsequent laboratory analysis. The procured tailings samples were prepared for the determination of the physical characteristics of tailings (i.e. bulk density, porosity, moisture content and specific gravity), geochemical characteristics (i.e. chemical elemental composition, paste pH and Eh), mineralogical analysis, batch leaching tests, sequential extraction scheme, and unconfined compressive strength test.

3.2.1. Sample preparation

Sample preparation forms a very important first step to all subsequent laboratory analyses. Tailings samples collected at each interval layer of the developed tailings profiles were prepared at the Department of Mining and Environmental Geology and at the Department of Ecological and Resource Management laboratories respectively, at the University of Venda.

Tailings samples from the respective tailings profiles were air dried at a room temperature (i.e. 22±2 ^{o}C). The samples were sieved using the basic sieve shaker (Retsch AS 200 model) to particle size less than 40 µm to ensure homogeneity. According to IMMSA (1980) more than 80 % of the concentration of potentially toxic metal and metalloids species is contained in the finest particles (<40 µm). After sieving and homogenizing, the tailings samples were transferred to sample bags and labeled according to depth intervals.

3.2.2. Physical characteristics

The physical properties of the tailings dump include bulk density, porosity, moisture content and specific gravity. The Bulk density was determined on air-dried samples using gravimetric technique from which porosity was calculated. Similar method was used by Sracek *et al*. (2010) on Cu and Co mine tailings at the Zambian Copper belt in the north of Zambia. The initial moisture content was determined as defined by the ASTM D 2216 (1998) by taking representative samples from each tailings profile. After determining their wet weight (total mass before heating or oven drying), these samples were oven dried at 105 ^{o}C for 8 hours, after which another weight measurement was taken (total mass after heating or oven drying). The difference between the two weights was taken as the initial moisture content or % moisture content.

Samples were oven dried at 105 ^{o}C for 24 hours followed by specific gravity tests determination according to ASTM D 854 (1998). Distilled water was used for these tests, and by gently rotating and agitating the flasks, it was assured that all air bubbles were eliminated from the samples before taking the weight measurements. Weight determinations were made using an electric balance sensitive to 0.01 g. A similar method was used by Mahmood and Mulligan (2007) when investigating the use of mine tailings for unpaved road base construction.

3.2.3. Chemical characteristics

The chemical characteristics of the tailings include bulk chemical composition, paste pH and Eh. Geochemical variables such as paste pH and Eh are very important factors that control the actual release of potentially toxic elements species from tailings to the environment.

3.2.3.1. Paste pH and Eh analysis

Tailings paste pH and *Eh* values were measured in a saturated soil paste using a combined *Thermo Scientific* instrument at the Department of Ecology and Resource Management, University of Venda. A saturated soil paste was prepared by adding 20 ml of distilled water to 20 g of air dried original sample (L/S ratio: 1:1). The slurry was mixed for 5 seconds and left to stand for 10 minutes. Romero *et al*. (2007) and Hiller *et al*. (2013) successively applied a similar method

3.2.3.2. Mineralogical and chemical elemental composition

The bulk chemical composition of the respective tailings samples was determined by X-ray fluorescence spectrometry (XRF) (Thermo Fisher ARL9400 XP+ Sequential XRF with WinXRF software) to determine the bulk chemical composition of major and trace elements within the characteristic zones of the developed tailings profiles.

Quantitative mineralogical analysis was performed using X-ray Diffraction Spectrometry (XRD) on tailings samples within the characteristic zones of tailings. The samples were analyzed using a PANalytical X'Pert Pro powder diffractometer in θ–θ configuration with an X'Celerator detector and variable divergence, and fixed receiving slits with Fe filtered Co-Kα radiation (λ=1.789Å). The phases were identified using X'Pert High score plus software. The relative phase amounts (weights %) were estimated using the Rietveld method (Autoquan Program). Polished thin sections from representative tailings profiles were prepared and carried out in reflected and transmitted light using a conventional petrographic microscope, to further reveal the mineralogical composition and transformation within the tailings samples at different characteristic depths. Scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS) (Leo1450 SEM, voltage was 10Kv, working distance 14mm) was performed to identify and understand the distribution of secondary mineral phases present at the tailings profiles.

3.2.4. Batch leaching test

The Musina area is a semi-arid (hot and dry) area with low precipitation ranging from 300 to 340 mm mostly in the summer season (Hemming, 2009). Consequently, the climatic conditions did not allow the extraction of pore tailings solution in the field, to evaluate the chemistry of aqueous tailings leachates a 10 g of the homogenized tailings samples was suspended in a 100 ml Mili-Q + deionized water (liquid/solid ratio of 1:10) in polyethylene plastic bottles. Sample suspensions were agitated in a shaker for 24 hours at a temperature of 22 ± 3 ^{o}C, at 200 rpm, until a stable reading of pH and electrical conductivity (EC) is obtained. After shaking, and pH and EC stabilization, the batches were centrifuged at 2,500×g for 20 minutes and filtered through a 0.45 µm membrane filter.

The clear aqueous extracts were divided into two subsamples. One set of samples were acidified to pH<2 with concentrated HNO_3 for cation analysis using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS), and the second set of samples was left un-acidified for anion analysis using Ion Chromatography technique (IC). Similar approach was successfully applied on abandoned Pb and Zn flotation tailings at 'El Fraile' impoundments in Taxco, central-southern Mexico, respectively (Lin, 1997; Romero *et al.* 2007). The analysis was performed in duplicates to validate the accuracy of the analytical results. The obtained concentrations of leachates were compared with the regulatory standards for drinking water quality as defined by the World Health Organization (WHO).

3.2.5. Sequential extraction

A few number of authors established that the total metal concentration in the waste provides inadequate information pertaining to their mobility and bioavailability, since not all forms of a metal are equally soluble (Tessier *et al*. 1979; Li and Thornton, 2001). However, the total metal concentrations do place an upper limit on metal bioavailability. Thus, to estimate the real mobility, bioavailability, and potential toxicity of heavy metals, it is important not only to determine their total concentrations but also the different chemical forms or ways of binding between major and trace metals and the solid phases of the sample (Joeng, 2003). Nevertheless, different sequential extraction procedures have widely been used to study the binding forms of metals and metal speciation in mine waste, soil and sediments (Tessier *et al*. 1979; Usero *et al.* 1998). However, most of them modified the basic procedure originally developed for sediments by Tessier *et al*. (1979).

In the present study, a seven-step sequential extraction scheme modified after Tessier *et al*. (1979) and Dold (2003) was performed on drilled tailings dump samples to better understand the mode of occurrence, mobility, bioavailability, and potential toxicity of potentially toxic or heavy metal species at different geochemical phases in the tailings dump and tailings/soil-interface. The retention mechanisms or geochemical controlling processes of potentially toxic elements or heavy metal species within the tailings and tailings/soil-interface would be elucidated. The following extraction scheme was used with the addition of the water soluble fraction. First, the water-soluble fraction was executed, followed by the exchangeable fraction, carbonate fraction, iron and manganese hydroxide associated fraction, organic and secondary sulfide fraction, primary sulfide fraction and residual or silicate fraction.

3.2.6. Common extraction procedures for extraction 1-7

The extraction was performed in 50 ml polyethylene centrifuge tubes. After extraction 1-6, the residue was separated from the extract by centrifugation at 2,500×g for 10 minutes, washed with 20 ml of Mili-Q + deionized water and filtered with 45 µm membrane filters. Both the supernatant and washed solutions were collected into acid-washed plastic bottles and stored at 4ºC in a refrigerator for multi-elemental analysis by ICP-MS. The analysis was performed in duplicates to validate the extraction results.

3.2.6.1. Step i: Water-soluble fraction

Two grams (2g) of tailings dump from the selected tailings profile samples was weighed into 50 ml centrifuge tubes, and filled to a 50 ml mark with deionized water. The mixture was subjected into a mechanical shaker for a period of 1 hour at room temperature and processed.

3.2.6.2. Step ii: Exchangeable fraction

About 20 ml of 1 M NaOAc buffer solution at adjusted to pH 8.2 with HOAC was added to the solid residue recovered from the first extraction. The mixture was subjected into a mechanical shaker for a period of 1 hour at room temperature and processed as set out in section 3.2.5.1. The 1M NaOAc leach at pH 8.2 was used to extract the metals bound to the exchangeable fraction according to the method described by Tessier et al., (1979) and Dold (2003). This leach was selected for the exchangeable fraction to overcome the drawback of 1M NH4-acetate at pH 5.0, which lead to the partial attack of the carbonate fraction at an acidic pH 5.0 (Dold, 2003).

3.2.6.3. Step iii: Carbonate fraction

About 40 ml of 1 M NaOAc solution adjusted to pH 5 with HOAc was added to the solid residue recovered from the second step to extract the carbonate bound metals. The mixture was subjected into a mechanical shaker for a period of 5 hours at room temperature and processed as set out in section 3.2.5.1. However, the carbonate bound metals were extracted by first removing the water soluble and exchangeable fractions, respectively.

3.2.6.4. Step iv: Reducible or Fe and Mn oxide and hydroxide associated fraction

The residue recovered from the previous step was extracted with 40 ml of 1 M $NH_2OH.HCl$ in 25% (v/v) HOAc solution at pH 2. The mixture was constantly agitated in a mechanical shaker for a period of 5 hours at 96 ºC and processed as set out in section 3.2.5.1.

3.2.6.5. Step v: Organic and secondary sulfide fraction

The residue recovered from the fourth step was extracted with 15 ml 30% H_2O_2 and 3 ml 0.02 M HNO_3 solutions at pH 2. The mixture was subjected into a mechanical shaker constantly agitated for a period of 5 hours at a temperature of 85ºC and processed as set out in section 3.2.5.1.

3.2.6.6. Step vi: Primary sulphide fraction

On this extraction step, 750 mg of $KClO_3$ and 15 ml of 12 M HCl solution was added to the residue recovered from the previous extraction, subsequently 10 ml of 4 M HNO_3 was added to the mixture, placed in water bath shaker at 90ºC for 20 min, and processed as set out in section 3.2.5.1.

3.2.6.7. Step vii: Residual or silicate fraction

The residue recovered from the sixth extraction was digested with a triple acid digestion of 2: 1:1 mixture of hydrofluoric acid, nitric acid and hydrochloric acid. A 2 ml of HF solution was added into the residue recovered from the sixth extraction and the mixture was subjected to a water bath shaker for 20 minutes at 90 ºC. The mixture was allowed to cool, and then further digested with aqua regia (10 ml HNO_3 + 10 ml HCl, for 6 hours at 90 ºC). The digested mixture was then filtered into centrifuge tubes as set out in section 3.2.5.1. A similar method was used on selected 2g dried weight tailings samples for total metal analysis or pseudo-total digestion. Total metal analysis or digestion was carried out to determine the total metal concentrations in tailings profiles samples. The ICP-MS analyzed the obtained multi-elemental concentrations, and were used to validate the percentage recovery during sequential extraction experiment.

3.3. Statistical analysis of data

Statistical program SPPS V17.0 Statistics software for Windows was used to appraise whole data obtained from the seven steps sequential extraction scheme with principal component analysis using Varimax rotation and Kaiser Normalization for the reduction of obtained data and extraction of small number principal components. This was done to characterize data with cluster analysis to better understand the relationship between the behavior of the element species, and the controlling factors that can be responsible for the distribution of element species using principal component analysis.

3.4. Unconfined compressive strength test

The chemical composition of the tailings (such as high concentration of silica, and substantial amounts of aluminium and iron), makes copper mine tailings excellent pozzolana material, and suitable admixture in cement mortars, for beneficial application within the construction industry, thereby mitigating their potential environmental impacts. As such, the following methods or experimental procedures were followed to determine the unconfined compressive strength for determination of copper tailings as sustainable construction materials:

Materials (conforming to IS: 40311988-Methods of physical tests for hydraulic cement)

- Pozzolana Portland Cement (PPC)
- Natural river sand (Procured from Dzindi River, Thohoyandou)
- Tailings dump (copper tailings procured at 2.5m depth from the respective tailings profiles).

3.4.1. Physical and chemical properties of copper tailings and Natural River sand

The copper tailings samples were procured from the abandoned Musina copper mine tailings dump drilled at a depth of 2.5 m with use of a hand auger driller. The natural river sand was procured from Dzindi River in Thohoyandou. An oxide analysis was performed on the procured copper tailings by X-ray fluorescence (XRF) to determine the pozzolanic properties or chemical composition of the tailings. Particle size distribution was performed on both the copper tailings and Natural River sand using sieve analysis in accordance with ASTM D 422 (1998).

3.4.2. Mixture proportion

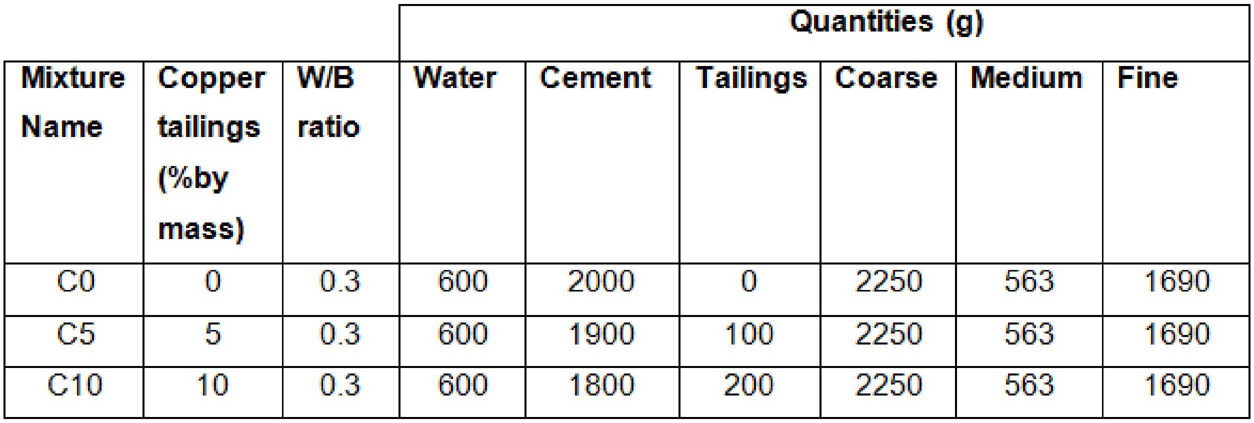
A 4500 g of the procured standard sand sieved at grade 1 (2mm-1mm and grade 2, coarse and medium) and grade 3 (1 mm-500 µm, fine particle size) was measured into an Erlenmeyer tray making 4500 g of sand, and subjected into a mechanical mixer.

Similarly, 2000g of cement was weighed and transferred into a mechanical mixer (combined weight of 6500g of cement and sand), mixed thoroughly in a dry state for 4 minutes before the addition of water (Fig.3.3). Subsequently, about 600g of water by weight of dry cement mix was added to the cement mix to get a cement paste, taking considering the settling time of water cement paste (3-5 minutes). The ratio of water to cement or binder (w/b ratio) was 0.3, and this mix was referred to as the control mix (C0).

Fig.3.3: Unconfined compressive strength procedures

Subsequently, about 5% (C5) and 10% (C10) dry copper tailings sieved at <90 µm of cement was added to the cement mortar mixture, respectively (Table 3.1). These cement mortar mix design were filled within the assembled mould with an area of 10000 m^2 (100mm x 100mm). A waste cloth was used to apply oil in the inner faces of the prepared moulds before they were filled with the respective cement mortar mixtures. After filling the moulds, they were then covered with plastic bag for 24 hours to maintain humidity at about 27±3ºC. After 24 hours of maintaining humidity, the cubes were then de-moulded and placed in water bath for curing or aging until 3 and 28 days respectively, as which the days required for the determination of their unconfined compressive strengths. The unconfined compressive strength on each prepared cube was measured using the unconfined compressive strength test machine which gives the maximum load and maximum strength after failure on each cube. The obtained crushing load or compressive strength value of each cube was compared with the control cement cube (C0) for the respective curing days (3 and 28 days) for the assessment of the improved compressive strength.

Table 3.1: Mixture proportion.



			Quantities (g)					
Mixture Name	**Copper tailings (%by mass)**	**W/B ratio**	**Water**	**Cement**	**Tailings**	**Coarse**	**Medium**	**Fine**
C0	0	0.3	600	2000	0	2250	563	1690
C5	5	0.3	600	1900	100	2250	563	1690
C10	10	0.3	600	1800	200	2250	563	1690

CHAPTER FOUR

RESULTS AND DISCUSSION 1

4.1. Physicochemical properties and mineralogical analysis of the drilled tailings samples

This chapter presents the results obtained from the macroscopic characteristics and physical properties of the drilled tailings samples. The mineralogical assemblage, bulk chemical element composition and pore-water chemistry of the tailings by depth are discussed. The physicochemical properties and mineralogical processes that control the mobility/sinking of potentially toxic or heavy metal species in the tailings by depth are elucidated.

4.1.1. Introduction

Tailings are mineral waste or solid waste residue generated during beneficiation and mineral processing of the mined ore during mining activities (Lottermoser, 2010). The generated tailings are mainly disposed on land-fill or tailings holding pond as tailings dumps, and are either acidic or alkaline in nature depending on the dominant characteristic mineralogical assemblage within the tailings dumps (Sracek *et al*. 2010; Hiller *et al*. 2013). The chemical interaction between tailings dump, ingressed oxygen and infiltrating rainwater would lead to the geochemical and mineralogical transformations within the disposed tailings dump (Romero *et al*. 2007). This is followed by mobility of the released or leached potentially toxic or heavy metals species adsorbed in a variety of mineral phases present within the tailings dump to the environment. However, the mobilization and transport of the leached potentially toxic or heavy metal species from tailings is mainly affected by the physicochemical properties of the tailings and mineralogy processes occurring within the tailings dump disposal (Hiller *et al*. 2013). The physicochemical properties of the tailings that may affect the transport and mobility of the leached potentially toxic or heavy metal species within the tailings can be the physical or chemical properties of the disposed tailings dumps (Lu *et al*. 2014; Sracek *et al*. 2010). The physical properties of the tailings may include bulk density, air-filled porosity, and moisture content. The chemical properties of the tailings may include paste pH and Eh, total concentration of elements, and the dominant mineralogical assemblage of the tailings. However, the mineralogical processes that can affect the mobility/sinking of leached trace metals when tailings dump interact with infiltrating rainwater and ingressed oxygen, are mineral precipitation-dissolution, sorption-desorption reactions, as well as redox (pH/Eh) reactions (Romero *et al.* 2007; Hiller *et al*. 2013). The mobility of the leached trace metals from solid phases of the tailings as a consequent of the chemical interaction between tailings dump, atmospheric oxygen and infiltrating rainwater, may eventually pose a serious environmental concern over time.

The present study is an attempt to characterize the physicochemical properties and mineralogical assemblage of the abandoned copper tailings by depth, to elucidate the geochemical processes that control the mobility/sinking of potentially toxic heavy species within the established tailings profiles. This information is crucial when determining the suitability of the copper mine tailings for the development of sustainable materials in the construction industry as part of the re-use approach management system for disposed tailings dumps.

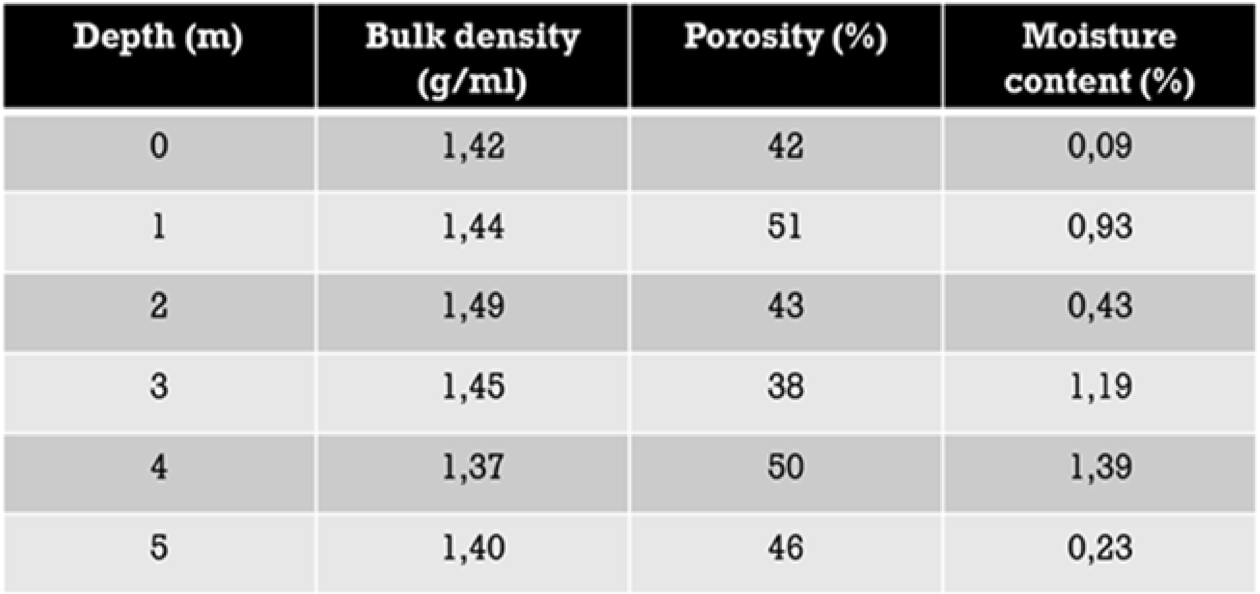
4.1.1.1. Macroscopic description and physical properties of samples

The procured tailings samples were uniform, varying less in color ranging from dark to light gray at shallow and deeper depths of the tailings, and dark to reddish brownish at the underlying soil or soil-interface. At tailings profiles A and B, the dark to light gray color of the tailings was continuous from a shallow depth of about 2.5 m to deeper zones of the tailings (≈ 3.5 m). At the base of the respective tailings profiles, there were spots of underlying soil ranging in color from light to dark brownish, indicating mixing with soil material below the mine tailings dump (≈ 4.5 m). Meanwhile, in tailings profile C the zone of contact with the underlying soil was reached at a shallow depth of about 2.5 m (Fig. 4.2 b.). Although, the water table was not reached along the respective tailings profiles, there was a layer of noticeable increased resistance to drilling at the upper and shallow depth of the tailings profiles, which was attributed to the presence of consolidated layer considering the climatic condition (semi-arid) of the Musina area. A Similar feature was noticed at a shallow depth of 0.9 m at the Chambishi site within the Zambian copperbelt, and was attributed to the presence of a cemented layer or hardpan (Sracek *et al*., 2010). The presence of hardpan or cement layers in a vertical profile have been reported to generally results in increasing bulk density and decreasing air-filled porosity in the tailings dump (McGregor and Blowes, 2002).

Fig.4.1: Procured tailings samples at different depth within the respective tailings profiles. The tailings range in color and grain size, from light-dark gray, medium to fine grain sandy material.

However, the physical properties of the tailings include bulk density, air-filled porosity, and moisture content. These physical properties of the tailings have a great relationship amongst each other, and regarded very important when understanding mobility controls of the leached potentially toxic or heavy metal species within the tailings depth and tailings soil-interface. Table 4.1 and Figure 4.2 below indicate the great relationship amongst the studied physical properties of the tailings, and how they control or affect the mobility of the leached potentially toxic or heavy metal species within the copper tailings by depth.

Table 4.1: Physical properties of the abandoned Musina copper tailings in profile B.



Depth (m)	Bulk density (g/ml)	Porosity (%)	Moisture content (%)
0	1,42	42	0,09
1	1,44	51	0,93
2	1,49	43	0,43
3	1,45	38	1,19
4	1,37	50	1,39
5	1,40	46	0,23

The vertical tailings profile B indicates a higher bulk density in the upper and shallow zone of the tailings reaching about 1.5 g/ml at a depth of 2 m (Fig. 4.2 a). A similar bulk density trend was observed at the Chambishi site within the Zambian copperbelt by Sracek *et al*., (2010). However, the bulk density then decreases slightly to 1.2 g/ml at about 5 m at the base of the tailings, where the mine tailings material is already mixing with the underlying soil. At the vertical tailings profile C, the bulk density trend was similar, and decreases to about 1.25 g/ml at the base of the tailings and soil-interface or underlying soil. As indicated in Table 4.1, the tailings material retains low moisture content throughout with tailings depth. The vertical porosity tailings profile B shows a slightly decrease in porosity at the deeper zone of the tailings reaching about 38 % at 3 m (Table 4.1). However, porosity slightly increases to about 48 % where the mine tailings are already mixed with the underlying soil, within the respective tailings profiles (Fig. 4.2 c, d). Nevertheless, the high bulk density and low porosity at the upper and shallow depths of the respective tailings profiles coupled with low moisture content could be attributed to the consolidated material commonly referred to as a cement (hardpan) layer. The semi-arid climatic condition of the study area corroborates this trend. Nevertheless, a large quantity of potentially toxic or heavy metals is anticipated to be incorporated within this zone or cement layer of the respective tailings profiles (Sracek *et al*. 2010; McGregor and Blowes 2002). The studied copper tailings have been exposed to oxidative weathering for a period of about (25 years), since the cessation of copper mining in 1995 (Cairncross and Dixon, 1995). Consequently, the presence of cemented layer in the upper and shallow zones of the tailings limited the penetration of oxidizing agents and oxidation products to un-oxidized tailings in the deeper zones of the tailings profiles.

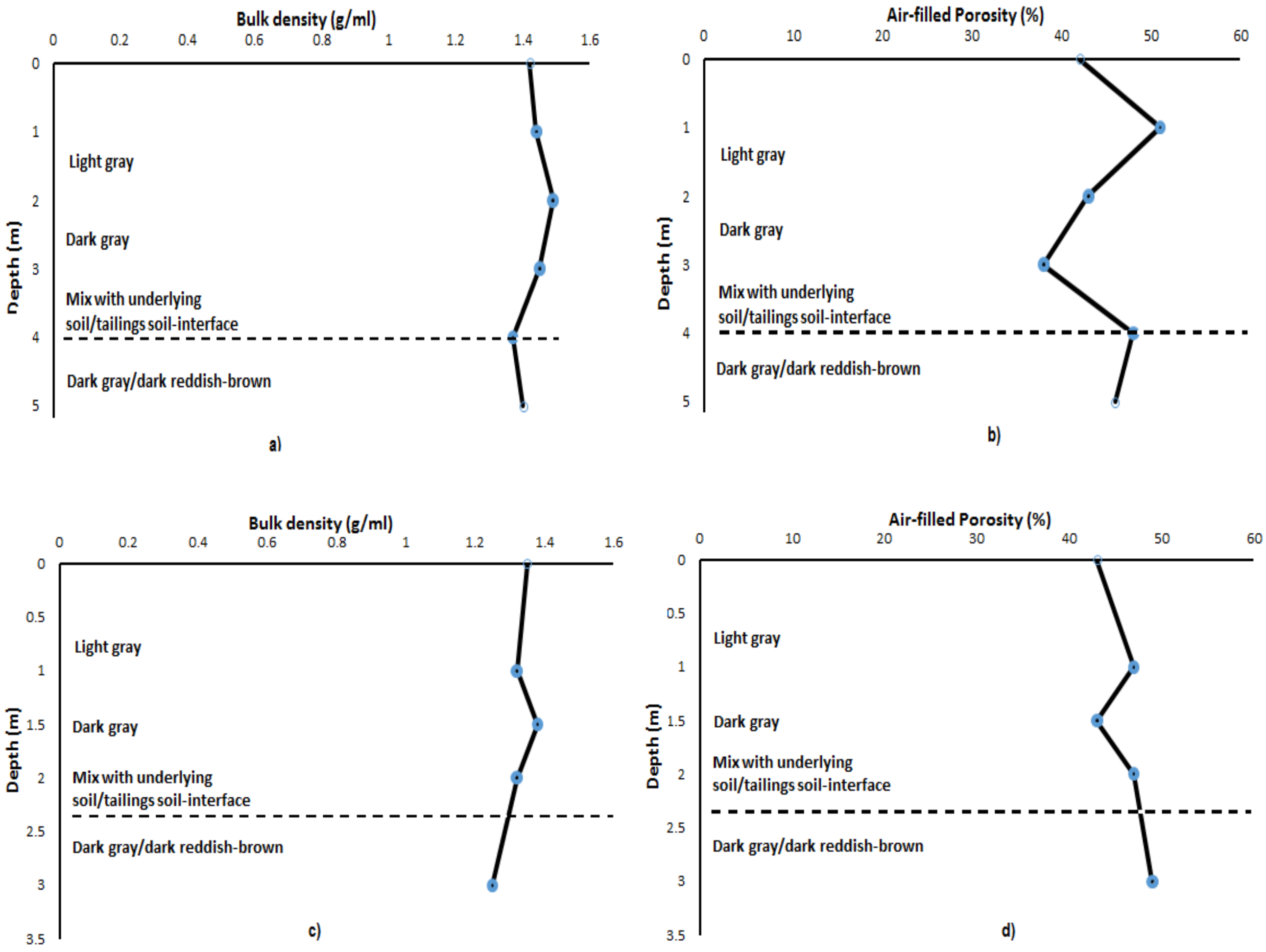


Fig. 4.2: Simplified vertical profiles for (a, b) Bulk density and Air-filled porosity in tailings profile B, and (c, d) Bulk density and Air-filled porosity in tailings profile C.

4.1.1.2. Mineralogical composition of the copper tailings

The obtained results from quantitative X-ray diffraction analysis of the drilled copper mine tailings samples are shown in Table 4.2 and the representative mineralogical composition trends with depth profiles are shown in Fig. 4.3. Fig. 4.4 indicates the representative microphotographs of thin sections. The qualitative X-ray diffraction spectra for drilled tailings samples along with SEM images are shown in Fig. 4.5 and Appendix B, respectively. The mineralogical compositional trends as a function of depth do not show any significant differences in the respective tailings profiles. The primary minerals are quartz, epidote, chlorite, plagioclase, and muscovite. On the other hand, calcite and hematite dominate the secondary mineral suite. The major mineral phase comprises of quartz, epidote and chlorite, meanwhile plagioclase, muscovite, calcite and hematite are present in minor quantities (Table 4.2). Similar mineralogical composition was observed by Sracek *et al.* (2010) on copper and cobalt mine tailings at the Chambishi and Mindolo site at the Zambian Copperbelt. Quartz was the most predominant gangue mineral within the respective tailings profiles, and its composition increased with increasing depth reaching about 42.4 wt. % and 42.95 wt. % at a depth of 5 m and 3 m in tailings profile B and C respectively, where the tailings are mixed with the underlying soil (Table 4.2 and Fig. 4.3). In tailings profile B, actinolite and plagioclase decreases with increasing depth, meanwhile chlorite, epidote, and muscovite have a uniform composition throughout the profile with depth (Table 4.2). The mineralogical composition of chlorite was high (16.7-18.87 wt. %) at the upper and shallow depth of the respective tailings profiles, although this mineralogical composition trend decreased abruptly (13.31-17.38 wt. %) towards the base of the respective tailings profiles, where the tailings are mixed with the underlying soil (Table 4.2 and Fig. 4.3).

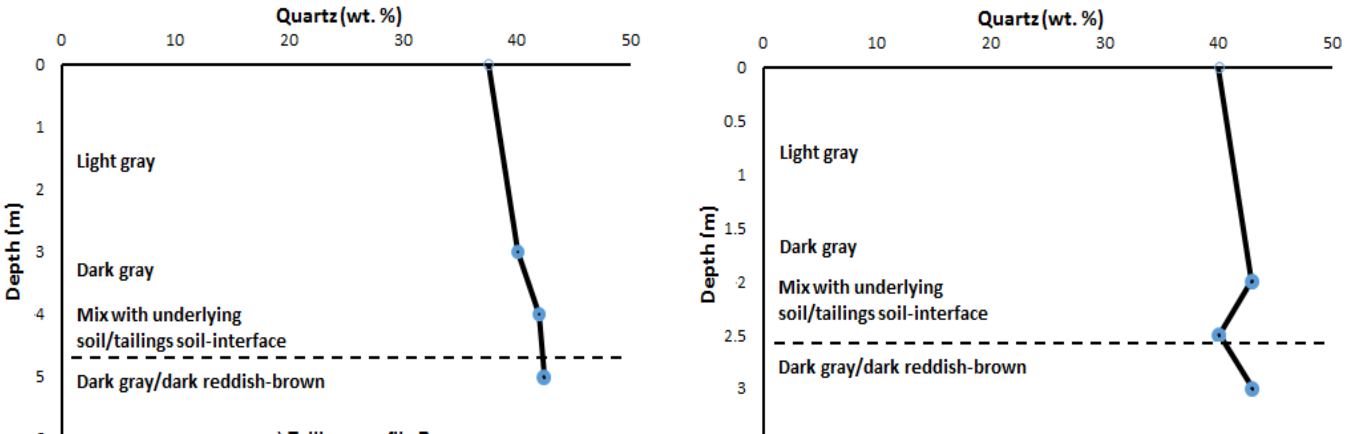
However, calcite was the only carbonate mineral identified by XRD analysis in the respective tailings profiles, and its trace composition increased with increasing depth from a low composition of 1.74 wt. % at the shallow or upper depth of tailings profile B to 2.24 wt. %, where the tailings are already mixing with the underlying soil or soil-interface (Table 4.2 and Fig. 4.3). A similar mineralogical composition trend was observed on tailings profile C (Fig. 4.3) Similarly, traces of hematite were identified by XRD analysis in both the respective tailings profiles, and its composition increased constantly to about 2.97 wt. % towards the base of the respective tailings profiles at the tailings-soil interface (Table 4.2 and Fig. 4.3). Relatively, hematite grain was observed by optical microscopy under plane polarized light occurring as coatings on the rims and corners of chlorite (Fig.4.4. b). Hematite is stable and very resistant to weathering processes, and has been reported to have the potential to incorporate large quantity of potentially toxic or heavy metals such as Cu, Co, Ni, Pb, and Cr (Lottermoser and Ashley, 2006).

Table 4.2: X-ray diffraction of bulk samples from tailings profile B and C.

Profile B (0-2m)	**Weight (%)**	**3 σ error**	**Profile B (2-4m)**	**Weight (%)**	**3 σ error**	**Profile B (5m)**	**Weight (%)**	**3 σ error**
Actinolite	4.12	0.87	Actinolite	3.08	0.93	Actinolite	2.97	0.9
Calcite	1.74	0.33	Calcite	1.79	0.36	Calcite	2.05	0.36
Chlorite	17.34	0.84	Chlorite	18.87	0.9	Chlorite	17.38	0.93
Epidote	21.64	0.99	Epidote	20.41	1.02	Epidote	21.61	1.05
Hematite	1.58	0.33	Hematite	1.76	0.36	Hematite	1.85	0.33
Muscovite	8.41	0.72	Muscovite	8.18	0.81	Muscovite	8.2	0.84
Plagioclase	7.65	0.9	Plagioclase	3.98	0.84	Plagioclase	3.54	0.72
Quartz	37.5	0.99	Quartz	41.92	1.08	Quartz	42.4	1.08
Profile C (0-2m)	**Weight (%)**	**3 σ error**	**Profile C (2m top-2m bottom)**	**Weight (%)**	**3 σ error**	**Profile C (3m)**	**Weight (%)**	**3 σ error**
Actinolite	4.1	0.9				Calcite	3.22	0.39
Calcite	2	0.39	Calcite	2.24	0.36	Chlorite	13.31	0.84
Chlorite	16.82	0.87	Chlorite	16.7	0.78	Epidote	19.94	0.93
Epidote	22.23	0.93	Epidote	23.56	0.87	Hematite	2.97	0.3
Hematite	1.62	0.3	Hematite	2.28	0.3	Muscovite	8.68	0.75
Muscovite	7.13	0.78	Muscovite	8.55	0.69	Plagioclase	6.64	0.87
Plagioclase	3.16	0.75	Plagioclase	6.59	0.75	Quartz	42.96	0.96
Quartz	42.94	1.05	Quartz	40.07	1.05	Actinolite	2.47	0.75

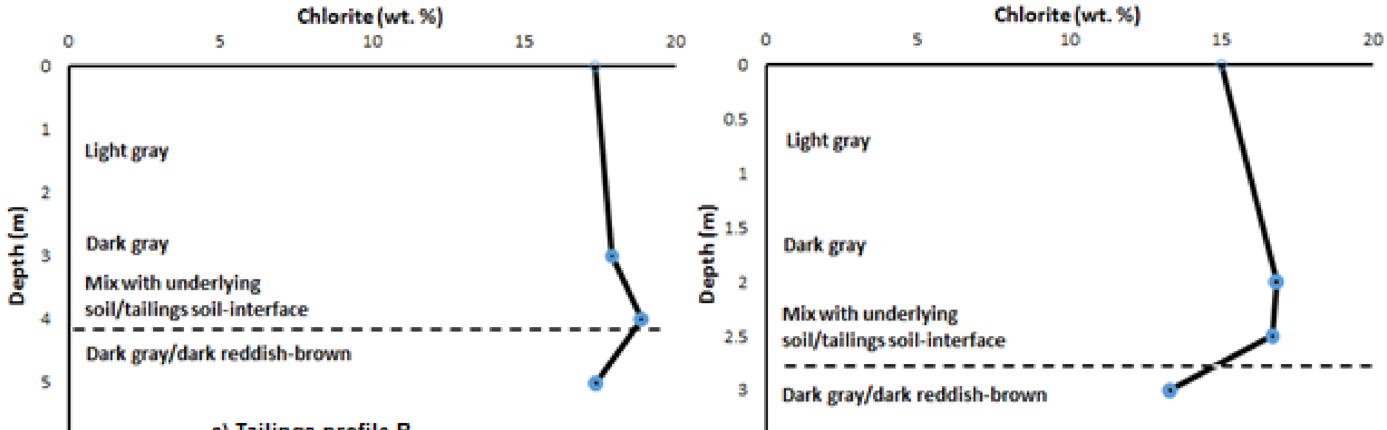
Generally, the mineralogical composition observed within the respective tailings profiles in the order of relative abundance is as follows: quartz>epidote>chlorite>muscovite>plagioclase>calcite>hematite. Similar mineralogical observations were made by Gitari *et al*., (2015) on the copper tailings at the same site. A significant relative abundance of potential acid neutralizers (such as calcite and alumino-silicate minerals) and the absence of primary sulphidic minerals suggests high neutralization capacity of the copper mine tailings, and consequently the severe environmental impact of the mine tailings will be moderated. Although, no primary sulphides were detected by X-ray diffraction analysis (Fig. 4.5), but discrete chalcopyrite grains were observed by optical microscopy under reflected polarized light (Fig. 4.4.a). The observed discrete chalcopyrite grains were attributed primarily to the mined ore (chalcopyrite, bornite and chalcocite) during past copper mining activities in Musina. However, the mineralogical transformation of chalcopyrite may not necessarily generate acidity when the disposed copper tailings dump chemically interact with atmospheric oxygen and infiltrating rain water, but will release significant amounts of potentially toxic or heavy metals such as Cu, Fe, and sulphates (SO_4^{2-}), to the tailings leachates and pore-waters, as described by the following chemical reaction:

$$CuFeS_2\ (s) + 4\ O_2 \rightarrow Fe^{2+} + Cu^{2+} + 2\ SO_4^{2-} \qquad \text{(Eq.12)}$$



a) Tailings profile B

b) Tailings profile C



c) Tailings profile B

d) Tailings profile C

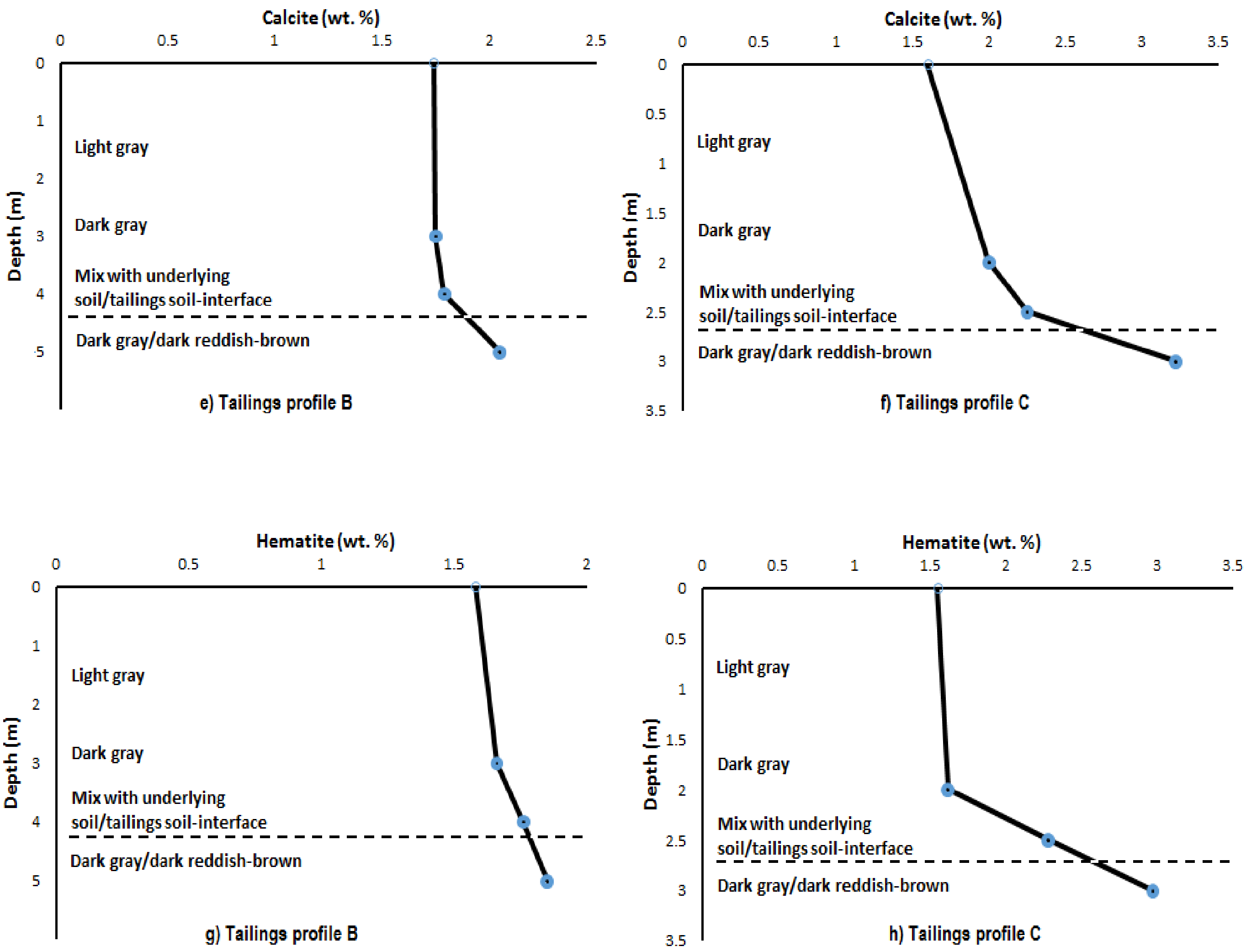


Fig. 4.3: Representative mineralogical composition trends with depth of the tailings from tailings profiles B and C, respectively.

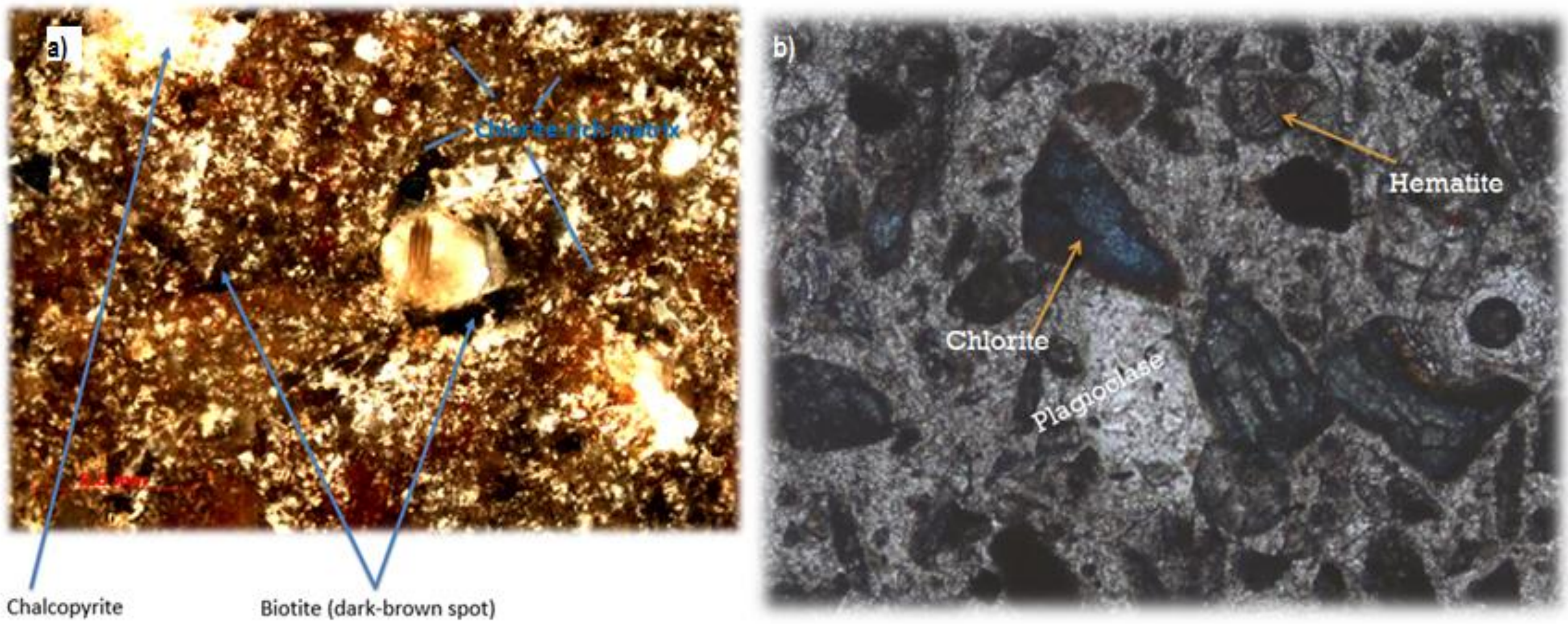
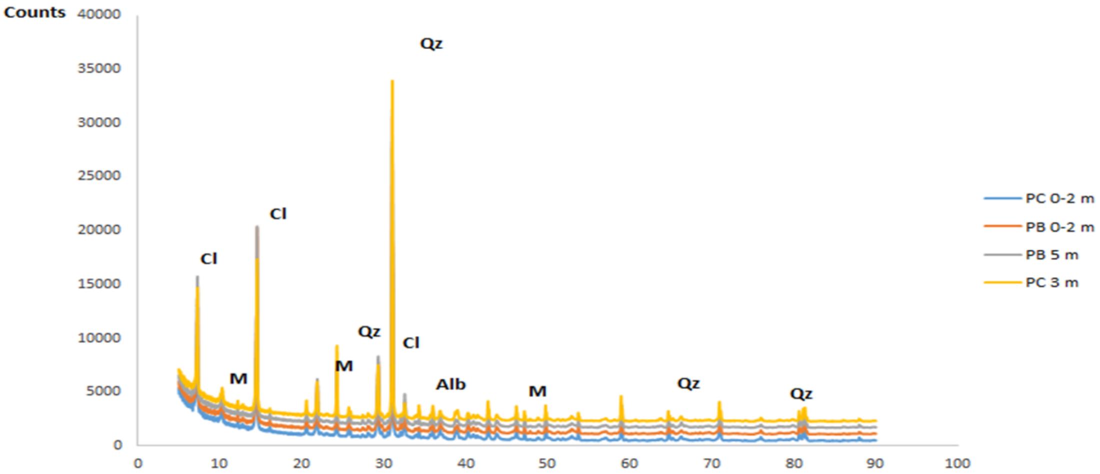
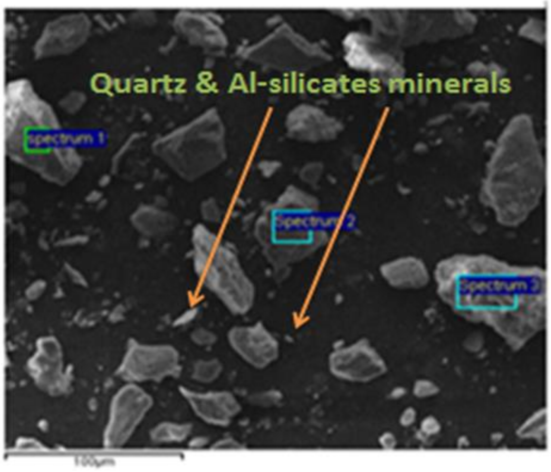
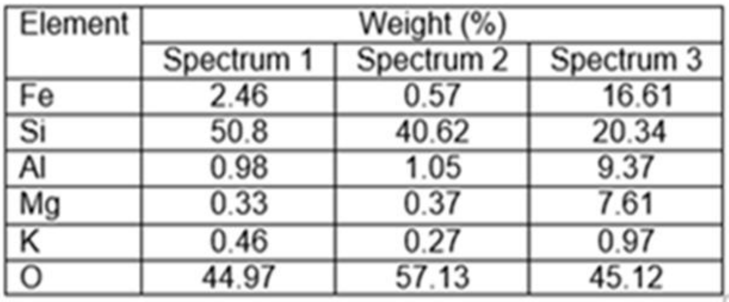


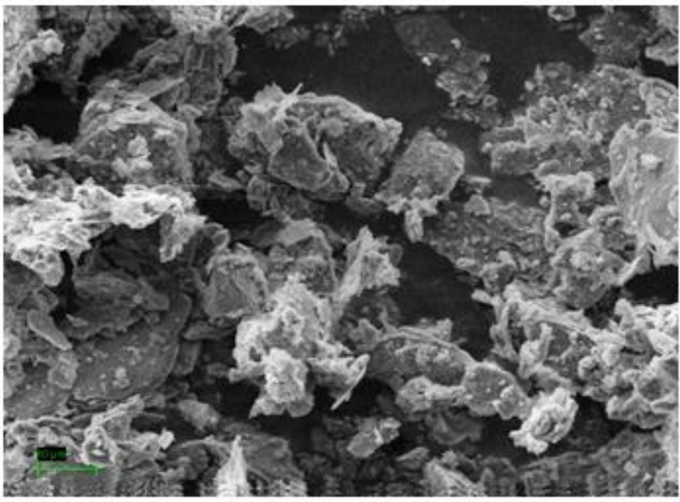
Fig. 4.4: Representative microphotograph of polished thin section a) under reflected polarized light and b) under plane polarized light at a shallow depth of about 2.5 m of tailings profile C.

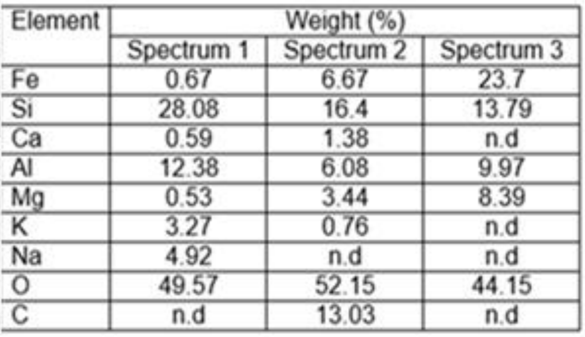






Element	Weight (%)		
	Spectrum 1	Spectrum 2	Spectrum 3
Fe	2.46	0.57	16.61
Si	50.8	40.62	20.34
Al	0.98	1.05	9.37
Mg	0.33	0.37	7.61
K	0.46	0.27	0.97
O	44.97	57.13	45.12





Element	Weight (%)		
	Spectrum 1	Spectrum 2	Spectrum 3
Fe	0.67	6.67	23.7
Si	28.08	16.4	13.79
Ca	0.59	1.38	n.d
Al	12.38	6.08	9.97
Mg	0.53	3.44	8.39
K	3.27	0.76	n.d
Na	4.92	n.d	n.d
O	49.57	52.15	44.15
C	n.d	13.03	n.d

Fig. 4.5: Representative SEM-EDS under 10 and 100 µm magnification and XRD patterns within profile C at a depth of 2.5 m. Abbreviations: Qz, quartz, Cl, clinochlore, M, muscovite, Alb, albite, *n.d* not detected.

Fig. 4.5 shows SEM-EDS analysis for the representative samples within tailings profile C by depth, validating XRD analytical results. The SEM microphotograph shows large silver white crystals surrounded by dark minerals which were identified as quartz and Al-silicate minerals, respectively. Nevertheless, EDS quantification showed that these mineral crystals are dominated by elements such as in average composition, O (48.91 wt. %), Si (28.32 wt. %), C (13.03 wt. %), Fe (11.03 wt. %), Al (6.63 wt. %), Na (4.92 wt. %), Mg (3.39 wt. %), K (1.29 wt. %), and substantial amounts of Ca (0.98 wt. %). The SEM-EDS results confirmed results observed from X-ray diffraction patterns which showed quartz and alumino-silicate minerals (epidote, plagioclase, chlorite, and muscovite) as the most abundant within the respective tailings profiles. The substantial quantity of Ca (0.98 wt. %) was attributed to the traces of calcite which was the only secondary carbonate mineral observed from XRD analysis. The high quantity of O (48.91 wt. %) and Fe (11.03 wt. %) was attributed to the formation of secondary phase like hematite, although its concentrations were very low within the respective tailings profile as indicated in the X-ray diffraction spectra.

4.1.1.3. Paste pH and Eh

Paste pH values are presented in Fig. 4.6 a) and b) for tailings profile B and C, respectively. The paste pH values were medium alkaline (7.97-8.37) for the respective tailings profiles. Similar paste pH values were observed in neutral, low sulphide/high carbonate tailings impoundment at eastern Slovakia (Hiller *et al*., 2013). The medium alkaline pH condition of the tailings is attributed to the dominant potential acid-neutralizers or pH buffering minerals, i.e. alumino-silicate minerals, and traces of carbonate (i.e. calcite) present within the tailings dump. The tailings pH content varies less with depth within the respective tailings profiles. At tailings profile B, paste pH increased from 8.0 at the upper zone reaching a maximum of 8.37 at a depth of 2.0 m within the shallow zone of the tailings profile, then slightly decreases with depth to about 7.97 towards the base of the tailings. Similar trends were observed at profile C, where the tailings pH was high reaching a maximum of 8.37, where the tailings are already mixed with the underlying soil. Nevertheless, as expected the measured paste Eh values were lower in both the respective tailings profiles (Eh = -90.8 to -61.9 mV) indicating a more reducing or anoxic geochemical environment (Table 4.3).

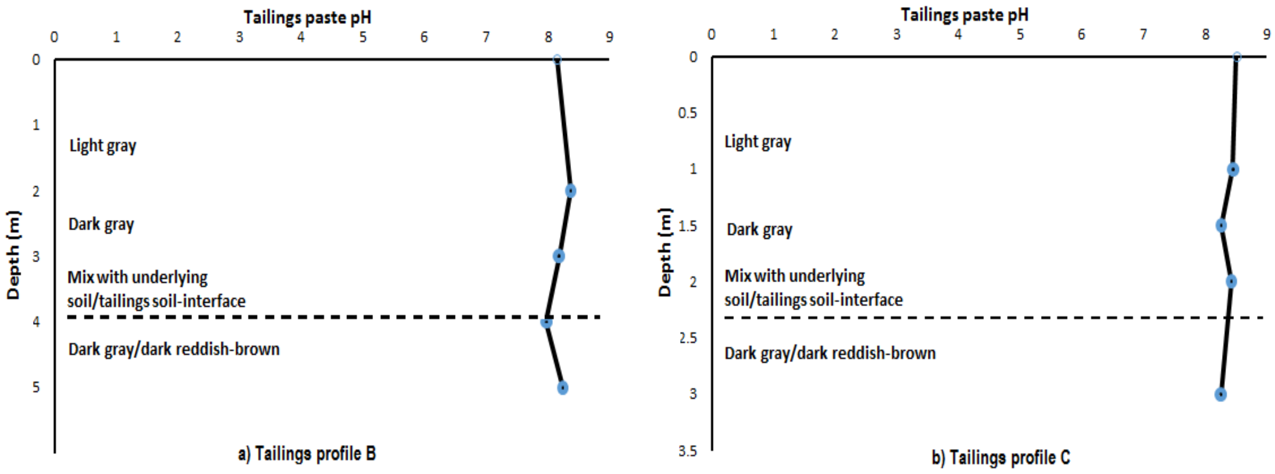


Fig. 4.6: Tailings paste pH content within the respective tailings profiles.

4.1.1.4. Total chemical element concentrations

The concentration of major and trace elements in the tailings samples are shown in Table 4.3 for tailings profile B and Appendix C1 for tailings profile C, respectively. The relative abundance of major elements is in the following order within the respective tailings profiles: Si>Al>Fe>Ca>Mg>K>Na. The concentration of these major elements agreed very well with the mineralogical composition of the tailings wherein quartz and alumino-silicates were the most abundant minerals within the established tailings profiles (Table 4.2). Silica concentration increased with depth in the respective tailings profiles in the same way as the quartz content which is the main carrier of Si in the tailings (Table 4.3 and Fig.4.3). The presence of other major elements such as Fe, Mg, K and Na corresponded obviously to the moderate presence of epidote, chlorite, muscovite, and hematite, whereas Ca was associated mainly with traces of calcite observed during mineralogical analysis (Table 4.2).

Table 4.3: Major and trace elements concentration in the tailings samples collected from tailings profile B.

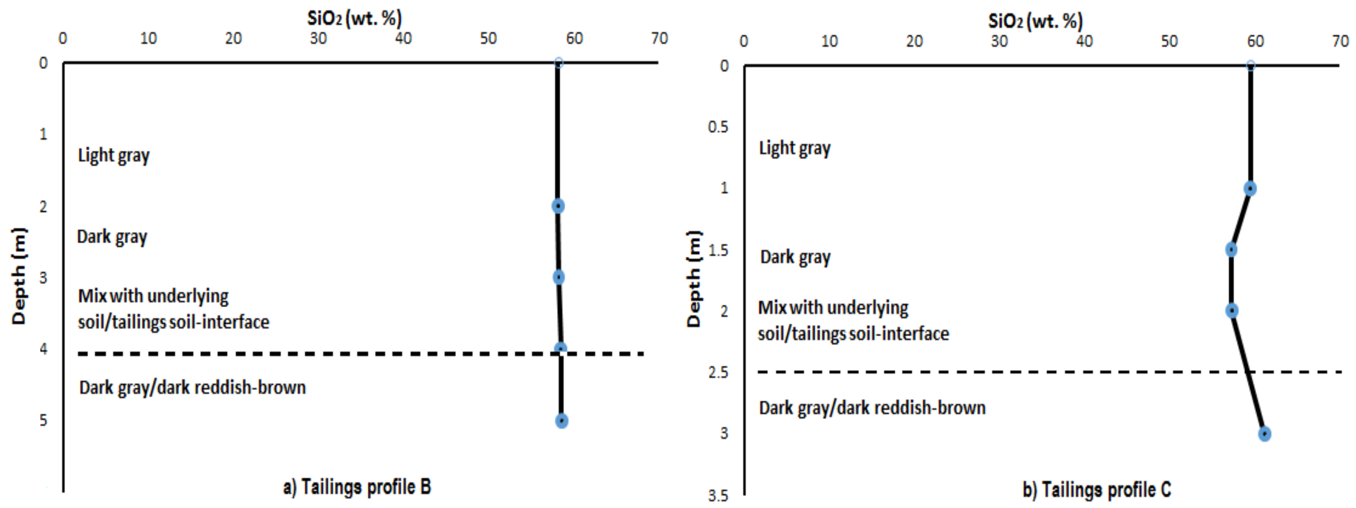
Paste pH	**8,14**	**8,37**	**8,18**	**7,97**	**8,24**
Eh (mv)	-71,3	-83,9	-73,3	-61,9	-77,2
Depth (m)	0-1	1-2	2-3	3-4	4-5
Color	Dark gray	Light/dark gray	Light/dark gray	Light/dark gray	Dark reddish-brownish
Wt.%					
LOI	9,93	3,23	2,96	3,08	2,89
SiO_2	58,12	58,14	58,25	58,49	58,58
Al_2O_3	14,17	13,98	13,96	13,93	13,56
Fe_2O_3	10,58	11,33	11,24	11,10	11,76
TiO_2	0,80	0,93	0,92	0,91	0,91
MnO	0,05	0,05	0,05	0,05	0,06
MgO	2,64	2,44	2,55	2,62	2,66
CaO	7,38	7,66	7,59	7,38	7,26
Na_2O	0,38	0,32	0,37	0,36	0,45
K_2O	1,02	0,86	0,83	0,86	0,81
NiO	0,02	0,01	0,01	0,02	0,02
ZrO_2	0,04	0,09	0,07	0,07	0,06
Total	99,55	99,51	99,18	99,27	99,41

ppm	**0-1 m**	**1-2 m**	**2-3 m**	**3-4 m**	**4-5 m**	**Canadian Soil Quality Guidelines (Industrial use)**
As	n.d	n.d	n.d	n.d	n.d	12
Cu	1063	862	602	816	515	91
Mo	n.d	n.d	n.d	n.d	n.d	-
Ni	36	16	20	35	14	50
Pb	n.d	n.d	n.d	n.d	n.d	600
Zn	25	13	15	24	10	360
Zr	151	223	187	256	123	-
Sr	236	192	197	252	133	-
Rb	8	n.d	n.d	6	n.d	-

Furthermore, the relative abundance of potentially toxic or heavy metal species is in the following order within the respective tailings profiles: Cu>Sr>Zr>Ni>Zn. Copper had the highest concentration amongst the potentially toxic or heavy metal species, reaching up to 1063 ppm at the upper zone of the tailings profile (Fig. 4.7). The elevated concentration of copper agreed well with the frequent presence of chalcopyrite within the tailings as shown in Figure 4.4. However, the elevated concentration of copper decreased moderately with depth, reaching 515 ppm where the tailings already mixed with the underlying soil or soil-interface (Fig. 4.7). Nevertheless, compared with the Canadian soil quality guidelines for the protection of the environment and industrial land use, copper (Cu) exceeded the guideline values by a large magnitude (Table 4.3). Some authors observed high concentration of copper (Cu) at a neutral, low-sulphide/high carbonate tailings at eastern Slovakia, and Chambishi site within the Zambian copperbelt, respectively (Matshusa and Makgae, 2014; Hiller *et al*. 2013; Sracek *et al*. 2010).

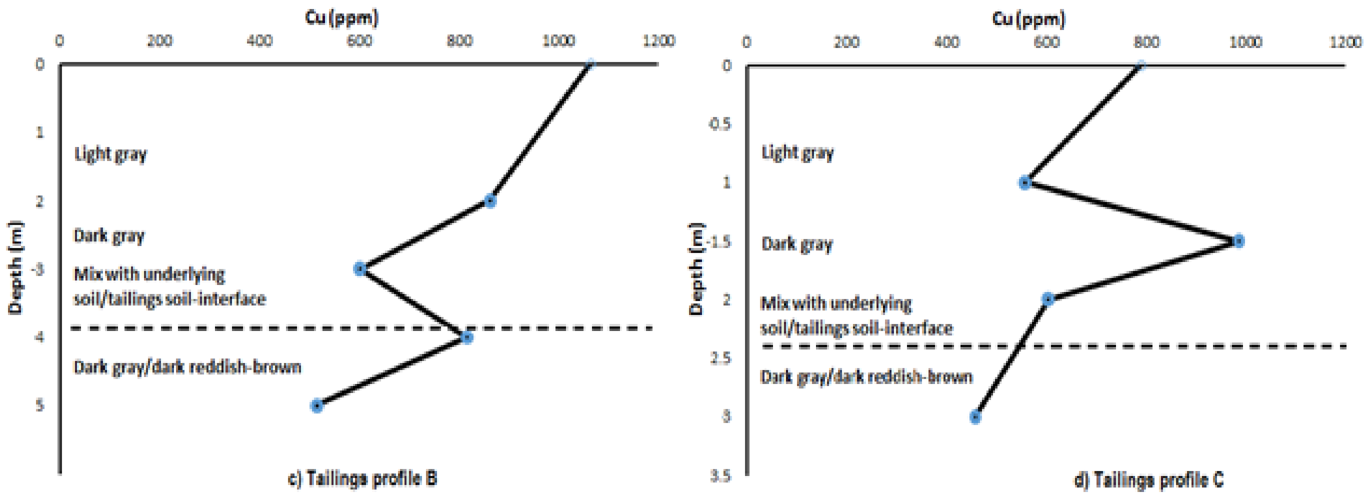
At elevated concentration, copper is known to have adverse environmental impacts mainly on plants and animals residing in nearby communities of the abandoned copper tailings dump. For example, the leaching of copper at elevated concentration from the disposed tailings dump may contaminate surface and groundwater systems thereby affecting the health of community feeding or depending on groundwater system as a source of water in the area. Moreover, elevated concentration of copper within the disposed copper tailings dump can reduce the agricultural capacity of the surrounding soil and destroy vegetation cover with the potential of soil erosion.

Thus, the elevated concentration of copper within the disposed tailings dump will require strategic monitoring or immobilization when considering the re-use of copper tailings dump disposal in either to sustain the construction industry or if rehabilitation is considered as part of the management approach system for tailings dump disposal. Nevertheless, moderate concentration of Zr, along with traces of Ni and Zn were also noticeable within the respective tailings profiles; however, their concentration did not exceed the Canadian guideline values for industrial land use.



a) Tailings profile B

b) Tailings profile C



c) Tailings profile B

d) Tailings profile C

Fig. 4.7: Representative chemical elemental composition of the selected major and trace elements with tailings depth within the respective tailings profiles.

4.1.1.5. Pore-water chemistry

Water soluble elements within the tailings are considered as more useful indicators of their potential hazards to the surrounding environment than total concentrations of the elements as water soluble elements are implicitly mobile and bioavailable (Hiller *et al*., 2013). The potential transfer of potentially toxic or heavy metals from tailings to water was evaluated using the standardized leaching test EN 12457-2 (2002), a similar approach was used by Romero *et al*. (2007) on abandoned Pb and Zn flotation tailings at ‘El Fraile’ impoundments in Taxco, central-southern Mexico. The obtained leachate concentrations of the potentially toxic or heavy metal species cations and sulphate anions were compared with the limit guideline values for drinking water quality prescribed by the World Health Organization (WHO) and the South African National Standard (SANS) as shown in Table 4.5 and Appendix D, respectively (Table C 1 for tailings profile C). Furthermore, the obtained leachate concentrations of potentially toxic or heavy metal species were used to understand their relative mobility and environmental bioavailability as a function of depth in the respective tailings profiles.

Nevertheless, comparison of the standardized leaching test results with the limit guideline values for the World Health Organization (WHO) and the South African National Standard (SANS), showed that only Al concentration were above the permissible limit (≤ 100µg/L) for drinking water quality in the respective tailings profiles. The average leachate concentration of Al (Aluminium) at the upper and shallow zones (0-2 m depth) reaches ≈235.85 µg/L, and decreases moderately to ≈100.54µg/L at the deeper zone (2-4 m) of the tailings, and slightly increases to an average of ≈134.35 µg/L at a depth of 4-5 m where the tailings are already mixed with the underlying soil, in the respective tailings profiles (Fig 4.8, Table 4.5 and Appendix D). Furthermore, the leachate concentration of Al coincides very well with the actual solid concentration of Al within the respective tailings profiles (section 4.1.1.4, Table 4.3).

The high concentration of Al (Aluminium) in the tailings leachate and pore water solution at the upper and shallow depths of the respective tailings profiles, was attributed to the neutralization and dissolution of the dominant Al-bearing silicate minerals (chlorite, plagioclase, and muscovite) identified by XRD analysis (Table 4.2). The dissolution of Al-bearing silicate minerals such as muscovite, results on the release of trivalent Al^{3+} cations in the leachate and pore water solution, generating neutral conditions in the tailings leachates and pore-water (Eq. 13).

$$KAl_3Si_3O_{10}(OH)_2 + 10H^+ \leftrightarrow K^+ + 3Al^{3+} + 3H_4SiO_4 \qquad \text{Eq. 13}$$

This is further corroborated by the medium alkaline tailings leachates pH (8.36-8.46), which corresponds very well with the medium alkaline tailings paste pH (7.97-8.37). Moreover, the tailings leachates pH is constant throughout the respective tailings depths (Table 4.5). Hiller *et al*. (2013) observed similar leachates pH trends on neutral, low-sulphide/high-carbonate tailings impoundment, at eastern Slovakia.

However, the average concentrations of other water soluble elements in the order of relative abundance are as follows: Fe>Cu>Mn>Zn>Ni>Pb (Table 4.5). The highest soluble concentrations for dissolved Fe (aver. ≈316.55µg/L) were observed at the upper and shallow zone (0-2 m) of the respective tailings profiles (Fig. 4.8). Nonetheless, this soluble concentration decreased slightly with tailings depth to an average of Fe ≈100.73µg/L towards the base of the tailings, where the tailings are already mixed with the underlying soil (Table 4.5 and Fig. 4.8). The dissolution of Fe-bearing silicate minerals (epidote and chlorite) identified by XRD analysis, was suggested to be the main source of high dissolved Fe concentrations in the respective tailings profiles.

Nonetheless, copper was the potentially toxic or heavy metal species that reached the highest water soluble concentration (≈25.65µg/L) at the upper and shallow depth (0-2 m), than that of Pb (0.27-0.34 µg/L), Ni (0.54-0.72 µg/L) and Zn (0.88-1.80 µg/L) in the respective tailings profiles (Table 4.5, Fig. 4.8 and Appendix D). The low soluble concentrations of dissolved Pb, Ni, and Zn in the tailings leachates and pore water was attributed to the medium alkaline pH condition of the tailings leachates and pore water (8.36-8.46), and the absence of soluble sulphide minerals hosting these trace metals. Furthermore, Dold (2005) reported that the solubility of many trace elements increases with decreasing pH, and more dissolved trace metals become mobile and bioavailable to the receiving surface and groundwater systems.

However, a better indication for the mobility of potentially toxic or heavy metal species can be obtained by the estimation of percentages leached of their total concentrations in the tailings (Table 4.4). Based on the calculated mobility percentage, the potentially toxic or heavy metal species showed low mobility, Ni (0.081 %), Cu (0.006 %) and Zn (0.05 %) on the upper and shallow depth of tailings profile B. The limited mobility of these potentially toxic or heavy metal species in these alkaline tailings results from the low solubility of secondary hematite mineral phase identified during mineralogical analysis (Table 4.2).

Table 4.4: Extractabilities of potentially toxic or heavy metal species expressed as the percentage leach of the total solid phase concentration within tailings profile B.

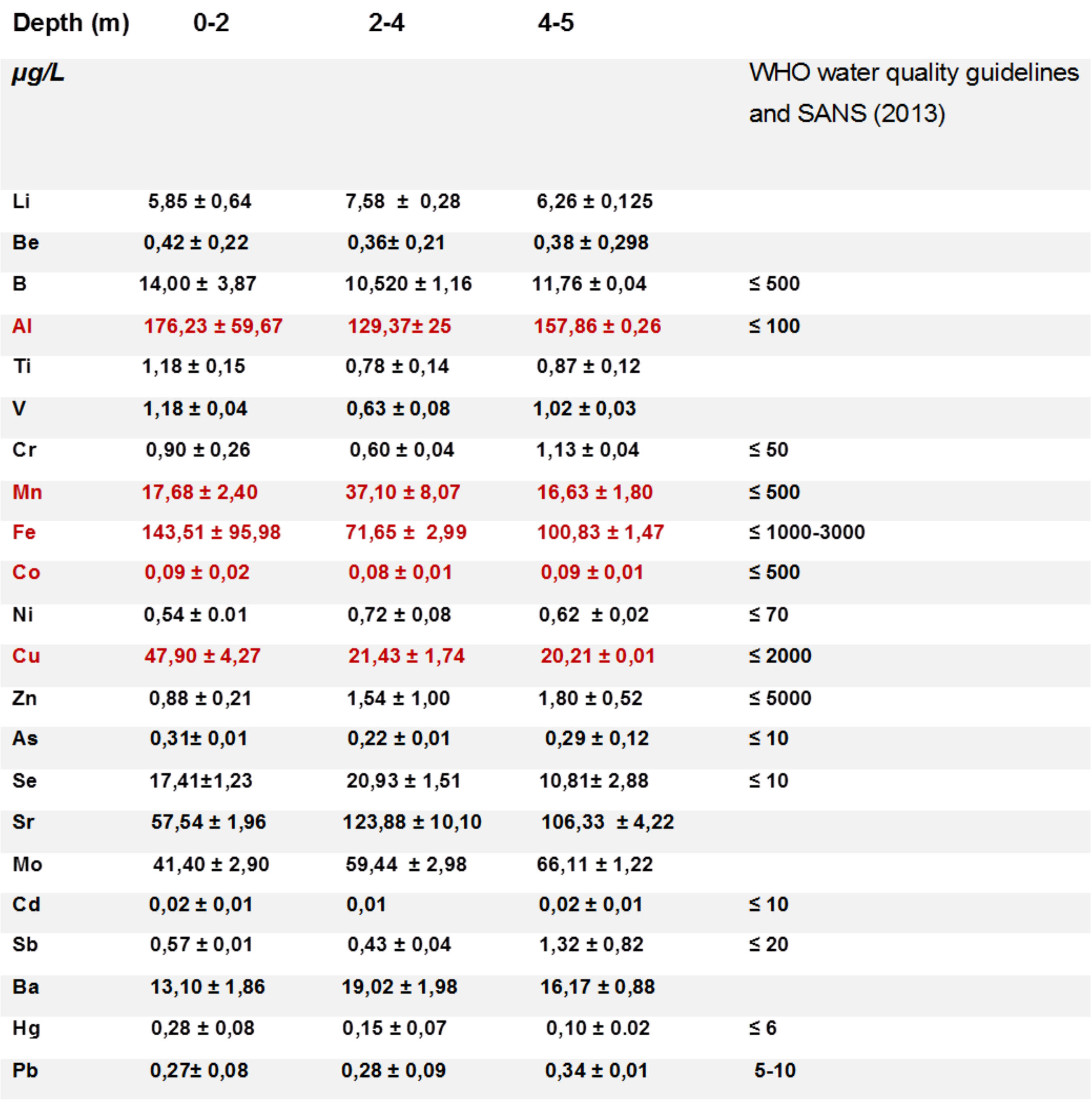
	Relative mobility or % leach of chemical species					
Sample Name	**Cu**	**Co**	**Ni**	**Cd**	**Zn**	**Pb**
PB (0-2 m)	0.006	*n.m*	0.081	*n.m*	0.005	*n.m*
PB (2-4 m)	0.003	*n.m*	0.003	*n.m*	0.015	*n.m*
PB (4-5 m)	0.005	*n.m*	0.006	*n.m*	0.027	*n.m*

n.m. not measured due to low detection limit of the solid phase

According to Sracek *et al*., (2010), hematite is very stable and resistance to dissolution, and incorporate large quantity of Cu and other potentially toxic or heavy metals. This is in good agreement with low pore-water concentration of potentially toxic or heavy metal species (Table 4.5). Furthermore, according to MINTEQA2 speciation calculations for the tailings leachates and pore-water, the tailings leachates and pore-water were oversaturated with regard to cuprite (SI = 1.403-5.488), and below saturation regarding oxyhydroxide minerals (Table 4.6). This shows that the formation of secondary cuprite (Cu_2O) is the other important factor controlling the solubility and mobility for Cu, Zn, and Ni in the respective tailings profiles. Moreover, the prevailing species of Cu were free Cu^{2+} ion (100%) in tailings profile B, and $CuSO_3^-$ (98.79%) in tailings profile C, suggesting the absence of ligands such as organic matter within the tailings samples which is further corroborated by the low Loss On ignition (LOI <10 %, Table 4.3).

Amongst the alkali earth metals, Ca had the highest water-soluble concentration, reaching ≈30.75 mg/l at the soil-interface (Table 4.5). The dissolution of secondary calcite mineral phase under alkaline pH conditions was suggested to be the main source of Ca (Calcium) in the tailings leachates and pore-water. Furthermore, amongst the anions, sulphates had the highest water-soluble concentration within the respective tailings profiles, and its solubility increased with increasing tailings depth averaging 87.76µg/L at the base of the tailings and where the tailings are already mixing with the underlying soil (Table 4.5 and Fig. 4.8). The high dissolved concentration of sulphates was attributed to the application of inorganic chemicals such as sulphuric acid during beneficiation and mineral processing of the mined ore.

Table 4.5: Mean concentration ± standard deviation (SD) of dissolved concentration of cations and anions within tailings profile B and C.



Depth (m)	**0-2**	**2-4**	**4-5**	
µg/L				WHO water quality guidelines and SANS (2013)
Li	**5,85 ± 0,64**	**7,58 ± 0,28**	**6,26 ± 0,125**	
Be	**0,42 ± 0,22**	**0,36± 0,21**	**0,38 ± 0,298**	
B	**14,00 ± 3,87**	**10,520 ± 1,16**	**11,76 ± 0,04**	**≤ 500**
Al	**176,23 ± 59,67**	**129,37± 25**	**157,86 ± 0,26**	**≤ 100**
Ti	**1,18 ± 0,15**	**0,78 ± 0,14**	**0,87 ± 0,12**	
V	**1,18 ± 0,04**	**0,63 ± 0,08**	**1,02 ± 0,03**	
Cr	**0,90 ± 0,26**	**0,60 ± 0,04**	**1,13 ± 0,04**	**≤ 50**
Mn	**17,68 ± 2,40**	**37,10 ± 8,07**	**16,63 ± 1,80**	**≤ 500**
Fe	**143,51 ± 95,98**	**71,65 ± 2,99**	**100,83 ± 1,47**	**≤ 1000-3000**
Co	**0,09 ± 0,02**	**0,08 ± 0,01**	**0,09 ± 0,01**	**≤ 500**
Ni	**0,54 ± 0.01**	**0,72 ± 0,08**	**0,62 ± 0,02**	**≤ 70**
Cu	**47,90 ± 4,27**	**21,43 ± 1,74**	**20,21 ± 0,01**	**≤ 2000**
Zn	**0,88 ± 0,21**	**1,54 ± 1,00**	**1,80 ± 0,52**	**≤ 5000**
As	**0,31± 0,01**	**0,22 ± 0,01**	**0,29 ± 0,12**	**≤ 10**
Se	**17,41±1,23**	**20,93 ± 1,51**	**10,81± 2,88**	**≤ 10**
Sr	**57,54 ± 1,96**	**123,88 ± 10,10**	**106,33 ± 4,22**	
Mo	**41,40 ± 2,90**	**59,44 ± 2,98**	**66,11 ± 1,22**	
Cd	**0,02 ± 0,01**	**0,01**	**0,02 ± 0,01**	**≤ 10**
Sb	**0,57 ± 0,01**	**0,43 ± 0,04**	**1,32 ± 0,82**	**≤ 20**
Ba	**13,10 ± 1,86**	**19,02 ± 1,98**	**16,17 ± 0,88**	
Hg	**0,28 ± 0,08**	**0,15 ± 0,07**	**0,10 ± 0.02**	**≤ 6**
Pb	**0,27± 0,08**	**0,28 ± 0,09**	**0,34 ± 0,01**	**5-10**

mg/L				
Ca	26,71 ± 0,707	55,515 ± 3,924	30,75 ± 2,07	≤ 150
K	9,09 ± 1,357	9,115 ± 1,916	8,45 ± 1,92	
Mg	4,88 ± 0,04	12,675 ± 1,77	8,01 ± 0,41	≤ 70
Na	2,085 ± 0,13	4,405 ± 0,205	4,88 ± 0,11	≤ 200
P	0,075 ± 0,007	0,06	0,06	
S	15,715 ± 0,035	55,945 ± 2,24	25,56 ± 1,98	
Si	3,41± 0,07	3,185 ± 0,06	3,59 ± 0,02	

Depth (m)	0-1	1-2	2-3	
pH	8,46 ± 0,098	8,365 ± 0,021	8,415 ± 0,049	
EC	156,5 ± 16,829	312 ± 7,071	364 ±1,414	
TDS	18,8	18,75 ± 0,0701	18,85 ± 0,071	
ppm				WHO water quality guidelines and SANS (2013)
SO_4^{2-}	13,028 ± 3,163	47,743 ± 0,937	87,768 ± 44,631	≤ 500
Cl^-	2,106 ± 0,355	16,936 ± 0,831	24,382 ± 0,445	≤ 300
F^-	0,784 ± 0,063	1,048 ± 0,348	0,791 ± 0,022	≤ 1.5

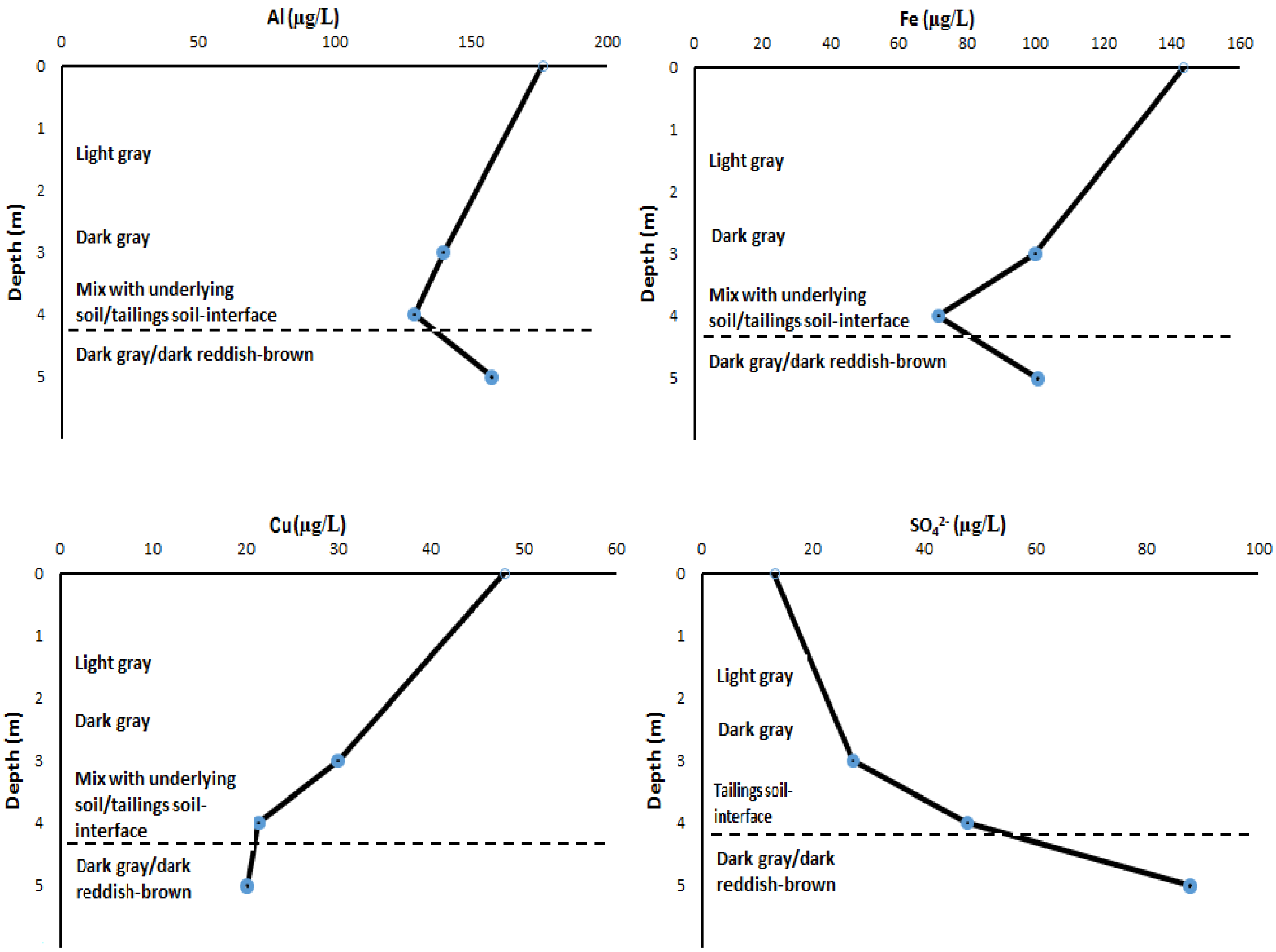


Fig. 4.8: Average tailings leachate concentration of selected metals as a function of depth within the respective tailings profiles.

Table 4.6: Saturation index of mineral phases (SI) and percentage of main species of potentially toxic or heavy metal species as calculated by MINTEQA2 for the tailings pore water sampled in tailings profile B and C, respectively.

	Profile B	**Profile C**
Saturation Index		
Cd (OH) $_2$ (s)	-7.074	-3.06
CoO (s)	-6.092	-5.605
Cr (OH) $_2$ (s)	-5.33	-5.022
Cuprite	5.488	1.403
Fe(OH) $_2$ (am)	-2.78	-2.453
Mg(OH)$_2$ (active)	-9.167	-8.453
Ni (OH) $_2$ (s)	-4.611	-4.06

Pb (OH) $_2$ (s)	-1.395	-1.017
Quartz	-2.925	-2.909
Zn(OH) $_2$ (am)	-4.171	-3.535
Main species (%)		
Cd		
Cd^{2+}	98.845	97.869
$CdOH^+$	1.145	2.013
Co		
Co^{2+}	96.854	94.082
$CoOH^+$	2.817	4.861
Co (OH)$_2$ (aq)	0.328	1.007
Cr		
Cr^{2+}	0.084	0.047
$CrOH^+$	99.916	99.953
Cu		
Cu^+	100	1.21
$CuSO_3^-$	N/A	98.79
Fe		
Fe^{2+}	94.508	90.637
$FeOH^+$	5.485	9.343
Mg		
Mg^{2+}	99.945	99.892
$MgOH^+$	0.055	0.098
Ni		
Ni^{2+}	97.992	96.181
$NiOH^+$	1.798	3.135
Ni (OH) 2 (aq)	0.21	0.65
Pb		
Pb^{2+}	20.695	12.434
$PbOH^+$	75.783	80.877
Pb (OH) $_2$ (aq)	3.517	6.672
Mn		
Mn^{2+}	N/A	99.309
$MnOH^+$	N/A	0.646
Na		
Na^+	100	99.999

4.1.2. Summary and conclusions

The studied tailings profiles are uniform, weakly altered, and show slight variations in bulk chemical and mineralogical composition with depth. The tailings profiles were characterized high bulk density and low air-filled porosity, as well as low moisture content at the upper and shallow zones of the tailings profiles. The precipitation of secondary mineral phases like hematite and calcite under medium alkaline geochemical condition led to the formation of cementations or consolidated materials within the upper and shallow zones of the respective tailings profiles. These cemented layers or consolidated material act as a trap or sink for the released potentially toxic or heavy metal species (up to 862 ppm of Cu, up to 36 ppm of Ni, and up to 25 ppm of Zn). This has led to the low concentration of these toxic or heavy metals (up to 515 ppm of Cu, up to 14 ppm of Ni, and up to 10 ppm of Zn) in the underlying tailings and tailings soil-interface. The tailings profiles were characterized by a medium alkaline paste pH (7.97-8.37) which corresponds very well with the tailings leachates or pore-water pH (8.36-8.46).

The relative abundance of the identified mineral peaks in the copper mine tailings samples followed the order: quartz>epidote>chlorite>muscovite>plagioclase>calcite>hematite, with alumino-silicate minerals being the most abundant within the respective tailings profiles. Chalcopyrite was the only primary sulphide mineral observed by optical microscopy. The high abundance of alumino-silicate minerals and traces of carbonates as calcite coupled with low sulphide mineral content, suggested a high neutralization capacity of the tailings, which agreed with their medium-alkaline pH nature. The main secondary minerals were calcite and hematite, and their proportion increased with tailings depth. In addition, they could retain relatively high amounts of potentially toxic or heavy metal (up to 862 ppm of Cu, up to 36 ppm of Ni, and up to 25 ppm of Zn) at the upper and shallow depth of the tailings, where bulk density was high and low porosity. Moreover, hematite formed coatings on the rims and corners of chlorite as observed from optical microscopy. The chemical composition of major elements within the respective tailings profiles followed the order: Si>Al>Fe>Ca>Mg>K>Na, and corresponds very well with the mineralogical composition of the tailings, where alumino-silicates were the most abundant minerals in the tailings samples. However, Al was the only major element exceeding the limit guideline values prescribed for drinking water quality.

Nevertheless, the relative abundance of trace elements contents in the copper mine tailings samples followed the order: Cu>Sr>Zr>Ni>Zn. Their concentrations decrease with increasing depth towards the base of the respective tailings profiles and soil-interface. This could be due to prevailing alkaline pH geochemical condition of the tailings. Nevertheless, the amounts of potentially toxic or heavy metals released into the solution were low; indicating that, presently, the tailings have a minor impact on heavy metals load transported to the receiving surface and groundwater systems.

The pH of tailings leachates and pore water suggest alkaline medium (8.36-8.46) and low concentrations of dissolved potentially toxic elements species (0.27-0.34 µg/L Pb, 0.54-0.72 µg/L Ni, 0.88-1.80 µg/L Zn, and 20.21-47.9 µg/L Cu), which decreased with increasing tailings depth. The low concentrations of dissolved potentially toxic elements species within the tailings leachates and pore water were even below the drinking water limits for these elements as defined by the World Health Organization (WHO). Based on MINTEQA2 calculation, cuprite (Cu_2O) was shown to be the most important solid phase controlling the mobility and sinking of Cu in the tailings leachates and pore water. Therefore, potential acid neutralizers such as alumino-silicates and calcite in addition to hematite, cuprite and pH within the respective tailings profiles, played an important role in the reduced dispersion of potentially toxic or heavy metal into the receiving surface and ground water systems.

CHAPTER FIVE

RESULTS AND DISCUSSION 2

SEQUENTIAL EXTRACTION SCHEME

This chapter presents experimental results obtained from the application of the sequential extraction scheme on old copper tailings dump, the sequential extraction scheme was modified after Tessier et al. (1979) and Dold (2003) for the speciation of particulate trace metals in different geochemical fractions or phases within the established tailings profiles. The effects of physicochemical properties and mineralogical transformation on the geochemical partitioning and distribution, potential mobility and environmental bioavailability of the potentially toxic or heavy metal species within the tailings and tailings soil-interface was elucidated.

5.1. Introduction

The risk posed by potentially toxic heavy metals and metalloids to the environment depend on their potential mobility and bioavailability (Joeng, 2003). Most studies dealing with particulate trace metals and metalloids species associated with the mine waste, suspended matter or bottom sediments in natural water systems are primarily concern with the measurement of the total concentration of particular trace metal and metalloids (Moncur *et al*. 2005; Romero *et al*. 2007; Hiller *et al*. 2013). However, the measurement of the total concentration of metal and metalloids species as a criterion to assess waste contaminations provide inadequate information pertaining to their mobility and bioavailability, since not all forms of a given metal and metalloid species are equally soluble in a solid waste (Tessier *et al.* 1979; Li and Thornton, 2001). Nonetheless, the total concentration of metal and metalloids species does place an upper limit on metal and metalloid species bioavailability (Dold, 2003).

Accordingly, to estimate the real mobility, bioavailability, and the danger that may be posed by potentially toxic metals and metalloids species on the receiving surface and groundwater systems, it is therefore important not only to determine their total concentration, but also the different chemical forms or ways of binding between trace metals and metalloids species, and the solid phases of the sample (Joeng, 2003). Elements are present in the soil or solid waste in different fractions like sulphides, sulphates, carbonates, silicates, oxides, and as native elements in minerals, that may strongly affect the way the element behaves in the particular soil or solid waste, depending on the elements mobility, bioavailability, toxicity and chemical interactions within the soil or waste (Arenas-Lago *et al*. 2014).

Nevertheless, in the present study, using fractionation methods based on sequential extraction technique, we need to establish how the potentially toxic or heavy metal species are geochemically partitioned and distributed in different geochemical fractions or phases within the tailings by depth. This is to better understand the component and physicochemical properties of the tailings that have the greatest influence on the retention of potentially toxic or heavy metals species within the drilled tailings profiles. This is carried out with special regard to their mobility, bioavailability and possible toxicity on the environment as pertains to surface and groundwater systems. The results shown for the tailings sample analysis are the average and standard deviation expressed on a dry material basis. Statistical program SPSS Statistics 19 was used for cluster analysis to better understand the origin or source and the relationship between potentially toxic element species, meanwhile principal component analysis was used to better understand the controlling factors that have the greatest influence on the retention of potentially toxic or heavy metal species within the tailings by depth.

5.2. Geochemical partitioning and mobility of potentially toxic or heavy metal species

A modified sequential extraction scheme was used to determine the geochemical partitioning of potentially toxic or heavy metal species in the dry disposed copper tailings dump. The experimental protocols of these results are presented in section 3.2.6. The geochemical partitioning of potentially toxic or heavy metal species such as Cr, Co, Ni, As, Cd, Pb, and Cu in different leachates extracted from different fractions within tailings profile B (2-4 m and 5 m) and tailings profile C (1-2 m and 3 m) are discussed, respectively. Table 5.1 shows the geochemical partitioning of potentially toxic or heavy metal species concentration in different fractions by depths within the respective tailings profiles. The cumulative concentration for the potentially toxic or heavy metal species at different depths was compared with the values from total acid digestion (Table 5.1). Table 5.2 shows the geochemical partitioning of major element species in different fractions by depths within the respective tailings profiles.

5.2.1. Water-soluble fraction

Heavy metals are simply a certain class of metallic elements. The human body requires trace amounts of some heavy metals for cellular functioning, including zinc, copper, iron, cobalt and others, but these can be dangerous at elevated or high concentration levels (Joeng, 2003). Other heavy metals such as mercury, lead, arsenic and cadmium have no known benefits and their accumulation over time can cause serious illness and even premature death (BRGM, 2002). Moreover, the industrialization of the world dramatically increased the overall environmental load of heavy metals (Lottermoser, 2010). Nevertheless, to understand the mobility patterns and potential environmental bioavailability of potentially toxic or heavy metal species in different geochemical fractions or phases of the tailings profiles, the water-soluble fraction was the first fraction to be submitted to sequential extraction scheme. The water-soluble fraction has been reported to contain metals derived from the re-dissolution of water soluble primary and secondary mineral phases (McGregor and Blowes, 2002).

Table 5.1 shows the geochemical partitioning of potentially toxic or heavy metal species at different depths within the fractions of the respective tailings profiles. From the sequential extraction scheme, the concentration of potentially toxic or heavy metal species (Cr, Mn, Co, Ni, Zn, As, Cd, and Pb) in the water-soluble fraction were very low (<0.1 mg/kg), except for Cu (0.09-0.27 mg/kg). The highest concentration of Cu (0.27 mg/kg) was partitioned in the upper and shallow depth (2-4 m) of tailings profile B (Table 5.1). Considerably, the total metal analysis or acid digestion concentration for Cu ranged between 360-675 mg/kg in the fractions of the respective tailings profiles (Table 5.1). The low concentration of potentially toxic or heavy metal species partitioned the water-soluble fraction is suggested to be due to the absence of highly soluble minerals such as sulphides hosting these trace metals in the tailings.

However, Table 5.2 shows the geochemical partitioning of major element species at different depths within the fractions of the respective tailings profiles. From the sequential extraction scheme in tailings profile B, Ca and Na have the highest concentration 43.61-56.67 mg/kg and 10.76-11.39 mg/kg, respectively. However, these concentrations slightly differ at the upper or shallow and deeper zones of tailings profile B, suggesting the high solubility of Ca and Na in the water-soluble fraction. The high concentration Ca was derived from pH-buffering reactions under alkaline pH conditions between the pore water and Ca-bearing carbonate phases such as calcite ($CaCO_3$) which was identified during mineralogical analysis (section 4.1.1.2).

Nevertheless, the concentrations of other major elements species such as Si (4.59-8.03 mg/kg), Fe (0.39-1.04 mg/kg), Mg (3.68-11.15 mg/kg) and Al (0.09-1.20 mg/kg) were very low in the water-soluble fraction, within the respective tailings profiles. The extracted concentrations of Fe and Al increases with tailings depth, reaching 1.04 mg/kg and 1.20 mg/kg at 5 m in tailings profile B (Table 5.2). Furthermore, it is suggested that the relatively low concentration of Fe in the water-soluble fraction is possibly due to the slower release or desorption due to the co-precipitation with secondary Fe-bearing hematite at favorable pore-water pH conditions.

5.2.2. Exchangeable and carbonate fraction

The exchangeable and carbonate fractions consist of metals that are readily available for uptake and potentially mobile into the environment (Tessier *et al*. 1979). These fractions are susceptible to pH changes, and metal release can be achieved through dissolution of a fraction of the solid material at low pH (Yuan, 2009). Tables 5.1 and 5.2 shows the geochemical partitioning of major and trace metals in the exchangeable and carbonate fractions by depth within the respective tailings profiles. Amongst the extracted potentially toxic or heavy metal species in these fractions, only Cu (0.07-321.75 mg/kg), Mn (0.16-10.48 mg/kg), Cr (0.04-0.42 mg/kg) and Ni (0.03-0.23 mg/kg) showed significant concentrations within the respective tailings profiles.

The concentration of Cu slightly differs with depth, with the highest concentration of Cu (321.75 mg/kg) recorded at the upper and shallow depth (2-4 m) of tailings profile B (Table 5.1). Comparatively, the concentration of Mn slightly differs with depth, with the highest concentration of Mn (10.84 mg/kg) recorded at the deeper zone (3 or 5 m) or tailings-soil interface (Table 5.1). The concentration differences for Cu and Mn in the upper or shallow depth (2-4 m) and tailings-soil interface (3 or 5 m) suggest that these potentially toxic or heavy metal species are released in the exchangeable and carbonate fractions within the respective tailings profiles. Furthermore, Table 5.1 corroborates the relative mobility of Cu and Mn, and this mobility is suggested to be controlled by the adsorption and desorption of these potentially toxic metal species due to variations in the pore-water pH condition.

Table 5.1: Geochemical partitioning of potentially toxic or heavy metal species in different fractions within the respective tailings profiles.

Sample	Fraction	Chemical species (mg/kg)								
		Cr	Mn	Co	Ni	Zn	As	Cd	Pb	Cu
PB (2-4m)	**F1**	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.26
	F2	0.00	0.16	0.01	0.03	0.00	0.00	0.00	0.00	0.89
	F3	0.42	6.24	0.09	0.14	0.00	0.00	0.01	0.03	321.75
	F4	2.94	7.45	0.39	0.91	1.46	0.10	0.02	1.34	172.05
	F5	1.51	2.70	0.37	0.31	0.43	0.00	0.00	0.11	34.57
	F6	2.40	5.15	0.47	0.89	0.25	0.22	0.00	0.94	16.28
	F7	248.36	261.10	8.08	65.08	40.73	5.51	0.03	16.93	37.59
	Sum of Fractions	255.90	282.83	10.22	67.36	42.87	5.83	0.06	19.35	583.39
	Pseudo-total digestion	248.00	272.91	16.14	73.54	58.67	6.40	1.02	22.14	595.71
	% recovery	102.80	103.60	63.32	91.96	73.06	91.00	5.88	87.39	97.90
PB (5m)	**F1**	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.27
	F2	0.00	0.17	0.01	0.00	0.00	0.00	0.00	0.00	0.26
	F3	0.41	10.15	0.15	0.23	1.51	0.00	0.01	0.03	263.91
	F4	2.94	7.45	0.39	0.91	1.46	0.10	0.02	1.34	172.05
	F5	1.51	2.70	0.37	0.31	0.43	0.10	0.00	0.11	34.57
	F6	4.05	7.53	0.69	1.63	1.27	0.29	0.01	1.97	38.45
	F7	248.36	335.81	27.42	89.92	37.00	6.23	0.03	6.61	116.85
	Sum of Fractions	257.27	363.83	29.03	93.01	41.67	6.72	0.07	10.06	626.36
	Pseudo-total digestion	268.39	378.98	28.00	93.54	52.21	7.44	0.08	12.26	675.86
	% recovery	95.85	96.00	103.67	100.00	79.81	90.32	87.50	82.05	92.67
PC (1-2m)	**F1**	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.09
	F2	0.00	0.10	0.01	0.01	0.00	0.00	0.00	0.00	0.07
	F3	0.09	9.59	0.13	0.23	0.45	0.00	0.02	0.19	165.28
	F4	0.60	4.85	0.18	1.03	0.95	0.05	0.01	0.97	65.08

	F5	0.47	1.35	0.15	0.29	0.24	0.00	0.00	0.03	13.84
	F6	3.01	7.44	0.57	1.46	0.59	0.36	< 0.5	6.86	37.43
	F7	90.74	152.89	11.96	33.60	33.60	3.06	3.98	3.98	58.92
	Sum of Fractions	94.91	176.24	13.00	36.63	35.83	3.47	4.01	12.03	340.71
	Pseudo-total digestion	94.67	269.93	15.31	44.33	38.07	2.11	5.02	12.33	360.90
	% recovery	100.20	65.29	84.91	91.72	94.11	164.45	79.88	97.56	94.40
PC (3m)	**F1**	< 0.02	0.04	0.00	0.00	< 0.2	0.00	< 0.05	< 0.05	0.15
	F2	< 0.02	0.15	0.01	0.00	< 0.2	0.00	< 0.05	0.00	0.61
	F3	0.04	10.84	0.10	0.16	0.25	< 3	0.02	0.03	120.28
	F4	5.31	8.60	0.38	0.94	1.52	0.08	0.02	1.12	160.20
	F5	1.82	2.72	0.41	0.37	0.46	0.00	0.00	0.06	75.18
	F6	4.26	5.94	0.62	1.32	0.48	0.29	0.01	1.46	28.48
	F7	236.24	337.27	26.60	91.84	36.35	6.05	0.06	6.82	110.33
	Sum of Fractions	248.05	365.56	28.12	94.63	39.06	6.42	0.11	9.49	495.23
	Pseudo-total digestion	244.67	369.93	43.09	75.91	49.23	8.50	1.02	10.83	424.79
	% recovery	101.38	98.81	65.25	124.66	79.34	75.52	10.78	87.62	116.58

F1: Water soluble fraction, F2: Exchangeable, F3: Carbonate fraction, F4: Fe and Mn hydroxide fraction, F5: Organic matter and sulphide fraction, F6: Primary sulphide fraction, F7: Residual or Silicate fraction.

However, amongst the major element species only Na^+ (39135.0-175648 mg/kg), Ca (223-324 mg/kg), Mg (13.22-47.30 mg/kg), and K^+ (19.12-23.06 mg/kg) had significant concentrations in the exchangeable fraction. Both Na^+ and Ca showed increasing response with increasing tailings depth in the exchangeable fraction within the respective tailings profiles (Table 5.2). The release of K and Na^+ in the exchangeable fraction can be attributed to the neutralization and partial dissolution of the dominant alumino-silicate minerals and carbonates such as calcite in alkaline solutions of NaOAc leach. Nonetheless, other major elements species such as Al and Fe were not extracted in the exchangeable fraction, despite their dominant chemical composition within the tailings (Section 4.1.1.4).

5.2.3. Fe and Mn hydroxide associated fraction

Table 5.1 depicts the concentrations of potentially toxic or heavy metal species in the Fe and Mn hydroxide associated fraction extracted with 1M $NH_2OH.HCl$ in 25% (v/v) HOAc leach at pH 2. Amongst the extracted concentrations of potentially toxic or heavy metal species, Cu have the highest concentration (172 mg/kg) in this fraction recorded at the deeper zone (5 m) of tailings profile B, and these concentrations was constant with tailings depth in the Fe and Mn hydroxide associated fraction. Comparatively, Mn had the highest concentration (8.60 mg/kg) recorded at the deeper zone (3 m) or where the tailings are already mixed with the underlying soil in tailings profile C, and this concentration was also constant with tailings depth.

Moderately, low concentrations of Cr (0.60-5.31 mg/kg), Ni (0.18-0.39 mg/kg), Pb (0.03-1.34 mg/kg), and Zn (0.95-1.46 mg/kg) were recorded in the upper or shallow and deeper zones of the respective tailings profiles (Table 5.1). Under acidic pH geochemical condition, these potentially toxic or heavy metal species become adsorbed into the surface areas of the precipitated Fe and Mn hydroxide or oxide such as hematite as identified during mineralogical analysis. However, Fe and Mn hydroxide fraction have been reported to have high affinity and greater adsorption capacity for the potentially toxic or heavy metal species (Hiller *et al.,* 2013). Nonetheless, any change in the redox potential may lead to the desorption of the previously sorbed potentially toxic or heavy metal species, thereby becoming more mobile and bioavailable to the receiving surface and groundwater systems (Vega *et al*.2010).

Table 5.2 depicts the concentrations for major element species in the Fe and Mn hydroxide associated fraction extracted with 1M $NH_2OH.HCl$ in 25% (v/v) HOAc leach at pH 2. Amongst the extracted concentrations of major element species, Na^+ has the highest extracted concentrations ranging between 965-3345 mg/kg in the respective tailings profiles. However, in tailings profile B, this concentration decreases from 3345 mg/kg at 2-4 m depth reaching 1440.0 mg/kg at 5 m, where the tailings were already mixed with the underlying soil (Table 5.2). Nonetheless, this trend is incongruent in profile C, wherein the concentration of Na^+ increases from 965.25 mg/kg at 1-2 m depth reaching 1320.75 mg/kg at 3 m depth at the tailings-soil interface (Table 5.3).

However, with regards to the concentrations of other major element species, Si ranges between 184-317.5 mg/kg, Fe 504-783.45 mg/kg, Ca 121-197 mg/kg, and these concentrations increases with depth in the Fe and Mn hydroxide associated fraction within the respective tailings profiles. The low amount of Fe and Mn extracted in this fraction was attributed to the resistance to dissolution of the most stable secondary Fe oxide phases such as hematite under acidic condition.

5.2.4. Organic matter, secondary and primary sulphide fractions

The organic matter and metals bound to secondary sulphide fractions were extracted with a hot 30% H_2O_2/HNO_3 leach at pH 2, to completely oxidize the secondary sulphide minerals. The concentration of potentially toxic or heavy metal species is high in this fraction, ranging between 13.84-75.18 mg/kg for Cu, 1.35-7.44 mg/kg for Mn, 0.06-6.86 mg/kg for Pb, and 0.47-4.26 mg/kg for Cr (Table 5.1). The high concentration of Cu (75.18 mg/kg) and Cr (4.26 mg/kg) was geochemically partitioned in the deeper zone (3 m) or tailings-soil interface in tailings profile C (Table 5.1). The concentration of other potentially toxic or heavy metal species including Cd, As, Zn, Ni, and Co was not significant in the respective tailings profiles due to the absence of soluble secondary sulphide minerals that host these toxic metal species (Table 5.1.). Despite the low organic matter content in the tailings dump as corroborated by the fairly low Loss On Ignition (<10 %, Section 4.1.1.4, Table 4.3), the relative high concentration of Cu, Mn, Pb, and Cr partitioned in this fraction suggests their high affinity for organic matter. Moreover, the organic matter can be degraded under oxidizing conditions leading to the release of soluble trace metals, although the organic fraction released is considered not to be bioavailable due to the fact that it is thought to be associated with stable humic substances that release small amount of trace metals in a slow manner (Filgueiras *et al*. 2002).

Nonetheless, a combination of $KClO_3$ and HCl leach was used to extract metals associated with primary sulphides. Chao and Sanzolone (1977) found the combination of $KClO_3$ and HCl leach to be an effective treatment in dissolving the primary sulphide minerals such as pyrite, chalcopyrite, galena, and sphalerite. The Cu extracted in the $KClO_3$ and HCl leach ranged between 16.38-38.45 mg/kg (Table 5.1). This indicate that chalcopyrite detected by optical microscopy, was greatly dissolved in $KClO_3$ and HCl leach.

However, the concentration of major element species was very high in the organic matter or sulphides bound fractions and followed the order: K (14.48-93162.3 mg/kg)> Al (40.15-3906.75 mg/kg)> Fe (15.49-2385 mg/kg)> Na (25.48-1745.3 mg/kg)> Ca (120.84-926.63 mg/kg)> Si (132-379.38 mg/kg)>,Mg (65.26-293.88 mg/kg) (Table 5.2). The high concentrations of Al (3906.75 mg/kg), Fe (2385 mg/kg), and Si (379.38 mg/kg) were recorded at the deeper zone (5 m) or tailings-soil interface of tailings profile B (Table 5.2). This suggests that the $KClO_3$ and HCl leach may have caused partial destruction of silicates along the corners, edges, and surfaces, resulting on the partial dissolution of Al-Ca-Mg-K silicates in these fractions. The application of hot 30% H_2O_2/HNO_3 leach at pH 2 to selectively dissolve organic matter and secondary sulphide fraction prior to the dissolution of primary sulphide fraction with $KClO_3$ and HCl leach, significantly distinguished between primary and secondary sulphides bound metals, which was important in understanding their mobility and retention within these fractions of the respective tailings profiles.

Table 5.2: Geochemical partitioning of major metal species in different fractions within the respective tailings profiles

Sample	Fraction	Chemical species (mg/kg)						
		Si	Fe	Al	Ca	K	Mg	Na
PB (2-4m)	F1	5.58	0.39	0.43	43.61	6.16	3.68	10.76
	F2	4.20	< 0.001	0.21	223.73	19.12	13.22	39135.00
	F3	22.80	34.79	24.86	744.61	23.93	9.18	133453.13
	F4	261.80	650.10	131.75	173.45	90.92	71.19	3345.00
	F5	273.12	94.26	86.16	185.71	18.21	65.26	203.60
	F6	132.83	1322.25	346.81	845.63	88950.00	187.81	26.20
	F7	143498.54	45269.91	5830.64	1580.14	7730.82	298.05	3560.26
	Sum of fractions	144198.87	47371.70	6420.86	3796.88	96839.16	648.39	179733.95
	Pseudo-total digestion	255693.47	514376.07	7421.89	4423.91	951236.01	726.21	181272.95
	% recovery	56.40	9.21	86.51	85.83	10.18	89.28	99.15
PB (5m)	F1	8.03	1.04	1.20	56.67	8.14	11.15	11.39
	F2	4.16	< 0.001	0.10	324.30	21.90	47.30	45408.75
	F3	28.69	32.36	29.24	1160.63	27.52	22.90	132281.3
	F4	368.20	783.20	198.25	197.25	91.10	102.07	1440.00
	F5	379.38	15.49	83.55	272.85	14.48	76.68	64.10
	F6	214.56	2385.00	535.06	891.06	89718.75	293.88	30.29
	F7	151703.00	58921.52	3906.75	1850.95	9165.77	316.98	3607.53
	Sum of fractions	152706.02	62138.61	4753.60	4753.71	99047.66	870.96	182843.36
	Pseudo-total digestion	159553.73	115992.71	5544.34	5691.68	911482.49	947.52	191326.85
	% recovery	95.71	53.57	85.73785	83.52	10.87	91.92	95.57
PC (1-2m)	F1	4.59	< 0.001	0.09	78.31	14.96	11.02	147.94
	F2	3.33	< 0.001	0.17	323.14	22.99	34.18	40380.00
	F3	22.67	25.73	26.59	1406.72	25.89	17.97	132328.13
	F4	184.94	504.05	78.17	121.04	83.40	51.26	965.25
	F5	171.36	17.28	40.15	120.84	8.84	30.72	41.42

	F6	174.69	2186.88	460.44	926.63	93162.50	251.88	40.16
	F7	78112.57	27753.45	3153.49	1188.68	4918.84	140.92	1745.30
	Sum of fractions	78674.15	30487.39	3759.10	4165.36	98237.42	537.95	175648.20
	Pseudo-total digestion	92711.75	43069.86	4226.72	5772.74	991431.60	656.75	201409.40
	% recovery	84.86	70.79	88.94	72.16	9.91	81.91	87.21
PC (3m)	**F1**	4.94	0.14	0.40	68.14	13.25	9.30	43.43
	F2	3.51	< 0.001	0.19	320.14	23.06	34.38	41373.75
	F3	19.81	20.71	20.23	1666.41	25.87	20.70	127500.00
	F4	317.50	692.45	167.20	147.90	93.40	94.66	1320.75
	F5	331.56	24.50	85.45	258.63	15.16	85.33	62.98
	F6	174.19	1705.50	423.56	898.56	91068.75	231.44	25.48
	F7	136549.57	56588.84	4383.97	2157.09	7704.92	211.88	4146.94
	Sum of fractions	137400.78	59032.14	5081.00	5516.87	98944.40	687.68	174473.33
	Pseudo-total digestion	264728.11	15055.83	7812.53	778.89	50665.50	765.96	181271.15
	% recovery	51.90	392.09	65.04	708.30	195.29	89.78	96.25

F1: Water soluble fraction, F2: Exchangeable, F3: Carbonate fraction, F4: Fe and Mn hydroxide fraction, F5: Organic matter and sulphide fraction, F6: Primary sulphide fraction, F7: Residual or Silicate fraction.

5.2.5. Residual or Silicate fraction

The residual or silicate fraction was submitted to triple acid digestion (HF with HCl/HNO_3 at a ratio of 2:1:1) to leach out metals that were strongly bound to the tailings and tailings soil-interface in the residual phase. The concentrations of potentially toxic or heavy metal species was very high in this fraction within the respective tailings profiles, Mn (152.89-337.27 mg/kg), Cr (90.74-248.36 mg/kg), Cu (37.59-116.85 mg/kg), Ni (33.60-91.84 mg/kg), Zn (33.6-40.73 mg/kg), Pb (3.98-16.93 mg/kg), and As (3.06-6.05 mg/kg) (Table 5.1). The higher concentration of Mn and Ni was recorded in profile C at 3 m depth, reaching 337.27 mg/kg and 91.84 mg/kg, respectively. Comparatively, the higher concentrations of Cu, Cr, and Co were recorded in profile B at 5 m depth, reaching 116.85 mg/kg, 248.36 mg/kg and 27.42 mg/kg, respectively (Table 5.1). This suggests that the silicate or primary and secondary minerals within the residual fraction retained relatively high quantity of potentially toxic or heavy metal species within their crystal structures (Okoro *et al.* 2012). This fraction is considered as the immobile fraction and the trace metals retained are not expected to be released into solution in the long term. However care must be taken since any change in the geochemistry (acidic pH conditions) may cause them to be displaced to more mobile fractions, thereby increasing their mobility and environmental bioavailability (Arenas-Lago *et al*. 2014).

However, the concentration of the major metal species was fairly high in this the residual or silicate fraction within the respective tailings profiles, Fe (27753.4-56588.84 mg/kg), Si (78112.57-151703 mg/kg), K (4918.84-9165.77 mg/kg), Al (3153.49-5830.64 mg/kg), Na (1745.3-4146.94 mg/kg), Mg (140.92-316.98 mg/kg), and Ca (1580.14-2157.09 mg/kg) (Table 5.3). The higher concentrations of Fe, Na, and Ca were recorded at the deeper zone (3 m) of tailings profile C, reaching 56588.84 mg/kg, 4146.94 mg/kg, and 2157.09 mg/kg, respectively (Table 5.2). Comparatively, the higher concentration of Si and Mg were recorded at the deeper zone (5 m) or tailings-soil interface of tailings profile B, reaching 151703 mg/kg and 316.98 mg/kg, respectively (Table 5.2).

Nevertheless, according to Margui *et al*. (2004), it is important to note that the geochemical partitioning of metals in the residual fraction largely depends on the metal content released in the previous fractions. Consequently, the low proportion of K and Na^+ in the residual or silicate fraction was attributed to high release of K and Na^+ on the prior carbonate, organic matter, primary and secondary sulphide fractions, whereby 14.48-93.162.3 mg/kg of K was released in the primary sulphide fraction due to the partial attack of the $KClO_3$ and HCl leach on the edges, corners and surfaces of the silicates, and 127500-133453.13 mg/kg of Na^+ was released in the carbonate fraction with the acidic NaOAc/HOAc leach (Table 5.2).

The high partitioning of Fe, Al and Mg in the residual or silicate fraction was attributed to the complete dissolution of predominant primary and secondary alumino-silicate minerals commonly in the form of epidote, chlorite, and muscovite as identified by XRD analysis (Table 4.2). Similarly, the high geochemical partition of Si in the residual fraction was attributed to the high mineralogical content of quartz (SiO_2) in the tailings samples which was detected during mineralogical analysis (section 4.2).

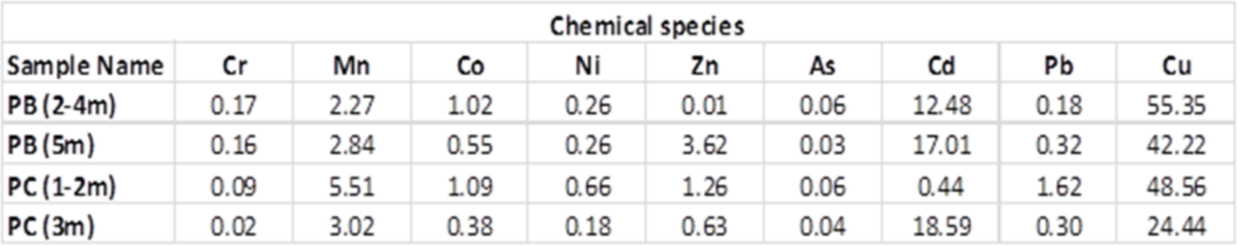
5.3. Major and trace elements distribution pattern in the fractions of the respective tailings profiles

The geochemical distribution pattern for major and potentially toxic or heavy metal species in different geochemical fractions or phases of the respective tailings profiles are presented in this section. The concentration of major and potentially toxic or heavy metal species in the extracted geochemical fractions or phases of the respective tailings profiles was calculated as a percentage distribution of the total metal content and the data obtained are presented in Figures 5.1-5.2 and Appendix E (Table E1 and E2) to show the relative values in different depth of the respective tailings profiles, the relative mobility or percentage leach of potentially toxic or heavy metal species is presented by Table 5.3, and Figure. 5.3 show SEM-EDS analysis validating sequential extraction scheme after the extraction of the Fe and Mn hydroxide associated fraction.

5.3.1. Water-soluble fraction

The water-soluble fraction includes weakly sorbed metals that are labile and can be easily leached and readily reach the environment when the disposed tailings dump is in contact with infiltrating rain water (Dold, 2003). Accordingly, the water-soluble fraction is the most active and mobile fraction with regard to environmental risk on surface and groundwater systems (Arenas-Lago *et al*. 2014). The amount and proportion of individual potentially toxic or heavy metal species leached in the water-soluble fraction is very small, and follows the order: Cu (0.03-0.04 %)> As (0.01-0.02 %)> Mn (0.01 %) (Fig. 5.1). It is suggested that environmental parameters, including the alkaline nature of the tailings and absence of soluble minerals within the tailings that host these toxic metals to be factors controlling the low geochemical distribution of potentially toxic or heavy metal species in the water-soluble fraction. Potentially toxic or heavy metal species are essential for living organisms and necessary in small amounts to ensure good health (WHO, 2003). Nevertheless, the lowest pools of potentially toxic or heavy metal species in the water-soluble fraction moderate their severity on the environment with regards to surface and groundwater systems.

Table 5.3: Relative mobility or % leach for the water-soluble, exchangeable and carbonate fractions (mobile fractions) with depth, in the respective tailings profiles.



	Chemical species								
Sample Name	Cr	Mn	Co	Ni	Zn	As	Cd	Pb	Cu
PB (2-4m)	0.17	2.27	1.02	0.26	0.01	0.06	12.48	0.18	55.35
PB (5m)	0.16	2.84	0.55	0.26	3.62	0.03	17.01	0.32	42.22
PC (1-2m)	0.09	5.51	1.09	0.66	1.26	0.06	0.44	1.62	48.56
PC (3m)	0.02	3.02	0.38	0.18	0.63	0.04	18.59	0.30	24.44

However, the proportion of major element species in the water-soluble fraction at different depths of the respective tailings profiles is shown in Figure 5.2 and Appendix E, Table E1. Comparatively, the percentage amount and proportion of individual major element species in the water-soluble fraction is very small. The relative percentage of major element species leached in the water-soluble fraction was in the following order: Mg (0.57-2.0 %)> Ca (1.15-1.88 %)> Na^+ (0.01-0.08 %). A noticeable proportion of Ca (1.88 %) in the water-soluble fraction was at the upper or shallow depth (1-2 m) in profile C. The proportion of Ca in the water-soluble fraction was suggested to be due to the partial dissolution of precipitated calcite ($CaCO_3$) under favorable conditions as identified during mineralogical studies (section 4.1.1.2.). The relative moderate proportion of Na^+ in the water-soluble fraction suggests that N^+ is water soluble.

5.3.2. Exchangeable and carbonate fractions

The exchangeable and carbonate fractions consist of metals that are readily available for uptake and potentially mobile into the environment (Tessier *et al*. 1979). These fractions are susceptible to pH changes, and metal release can be achieved through dissolution of a fraction of the solid material at low pH (Yuan, 2009). The percentage amount and proportion of potentially toxic or heavy metal species in the exchangeable fraction followed the order: Cu (0.02-0.12 %)> Mn (0.04-0.06 %)> Co (0.03-0.09 %). The low geochemical distribution of potentially toxic or heavy metal species in the exchangeable fraction was suggested to be affected by the alkaline pH of the extractant used to leach metals associated with the exchangeable fraction. The alkaline pH of the extractant used to leach potentially toxic or heavy metal species in the exchangeable fraction resulted in the low mobility of most of the potentially toxic or heavy metal species (Cr, Ni, Zn, As, and Pb) in this fraction (Table 5.3). Considerably, the contributions of potentially toxic or heavy metal species in the carbonate fraction revealed percentage leached in the following order: Cu (32.35-55.15 %)> Cd (0.44-1.77 %)> Mn (2.20-5.44 %)> Zn (0.63-3.61 %)> Co (0.35-1.03 %) (Fig.5.1). A rather shift or change in pH condition of the extractant used in the carbonate fraction as a function of 1M NaOAc adjusted to pH 5.0 with HOAc leach resulted on the quick release, and increased solubility and mobility (Table 5.3) of these potentially toxic or heavy metal species locked in different physicochemical forms in the carbonate fraction. The low pH or acidic geochemical condition of the solution will cause the potentially toxic or heavy metal species to be released through the dissolution of solid mineral phases (e.g. cuprite) hosting these potentially toxic metal species.

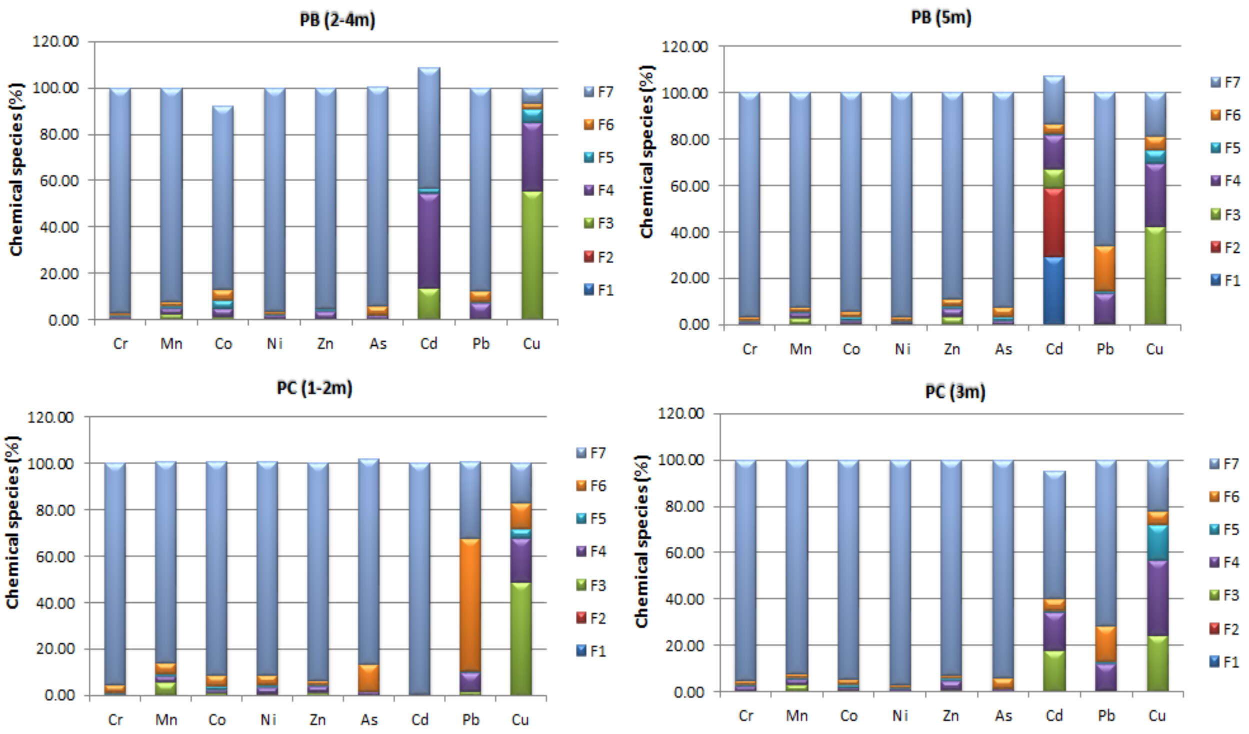


Fig. 5.1: Geochemical distribution of potentially toxic or heavy metal species extracted in different geochemical fractions or phases of the respective tailings profiles B and C, respectively (F1: Water soluble fraction, F2: Exchangeable fraction, F3: Carbonate fraction, F4: Fe and Mn hydroxide fraction, F5: Organic matter and secondary sulphide fraction, F6: Primary sulphide fraction, F7: Residual or Silicate fraction).

However, the geochemical distribution pattern of major element species in the exchangeable and carbonate fractions are shown in figure 5.2 for the respective tailings profiles. The relative proportion of major element species in the exchangeable fraction follows the order: Na^+ (21.77-24.83 %)> Ca (5.89-7.76 %)> Mg (2.04-6.35 %). The proportion of other major element species such as Si, Fe, Al and K was <1 %, suggesting the low exchangeable capacity of the tailings. Comparatively, the geochemical distribution of major elements in the carbonate fraction of the respective tailings profiles followed the order: Na^+ (72.35-75.34 %)> Ca (19.61-33.77 %)> Mg (1.42-3.34 %). The high geochemical distribution of Na^+ in the carbonate fraction indicate the partial attack on the edges and corners of plagioclase minerals identified during mineralogical studies (section 4.1.1.2). The slightly high percentage distribution of Ca in the carbonate fraction indicates the role of Ca in the precipitation of calcite ($CaCO_3$) in the respective tailings profiles.

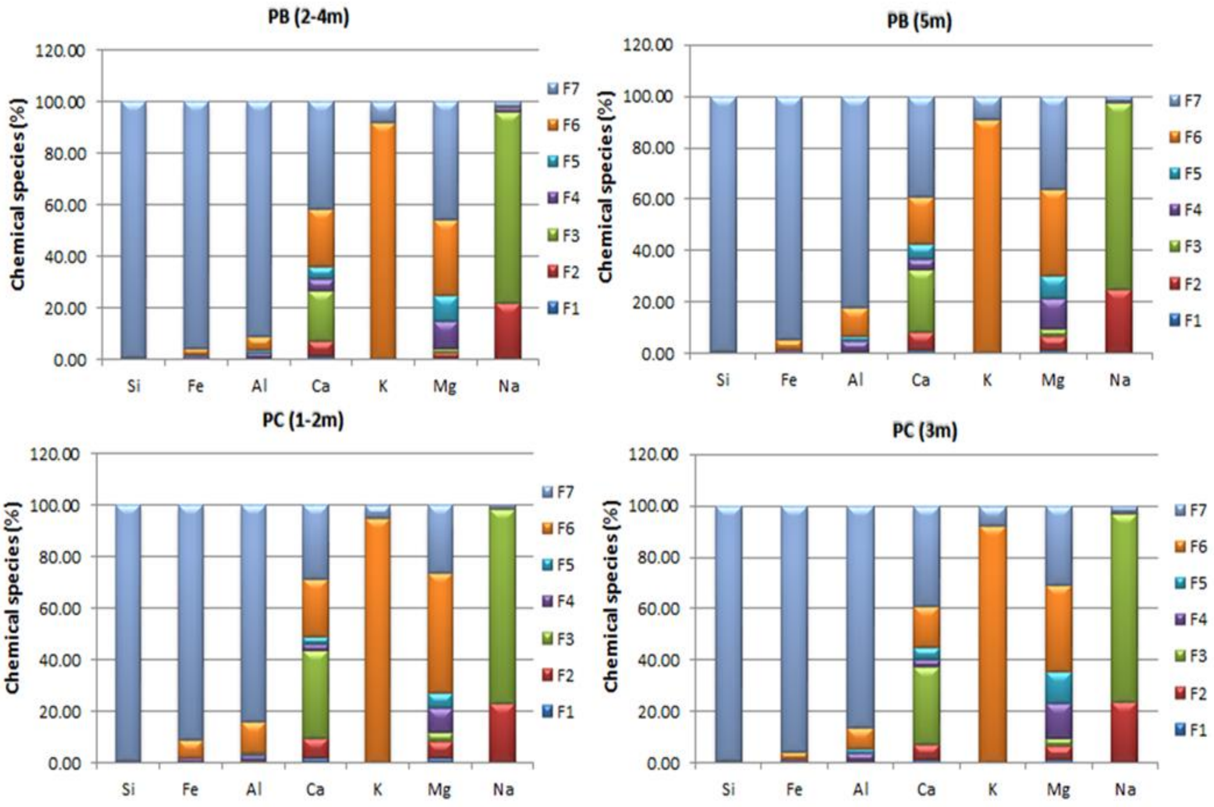


Fig. 5.2: Geochemical distribution pattern for major elements species in the fractions of the respective tailings profiles (F1: Water soluble fraction, F2: Exchangeable fraction, F3: Carbonate fraction, F4: Fe and Mn hydroxide associated fraction, F5: Organic matter and secondary sulphide fraction, F6: Primary sulphide fraction, F7: Residual or Silicate fraction).

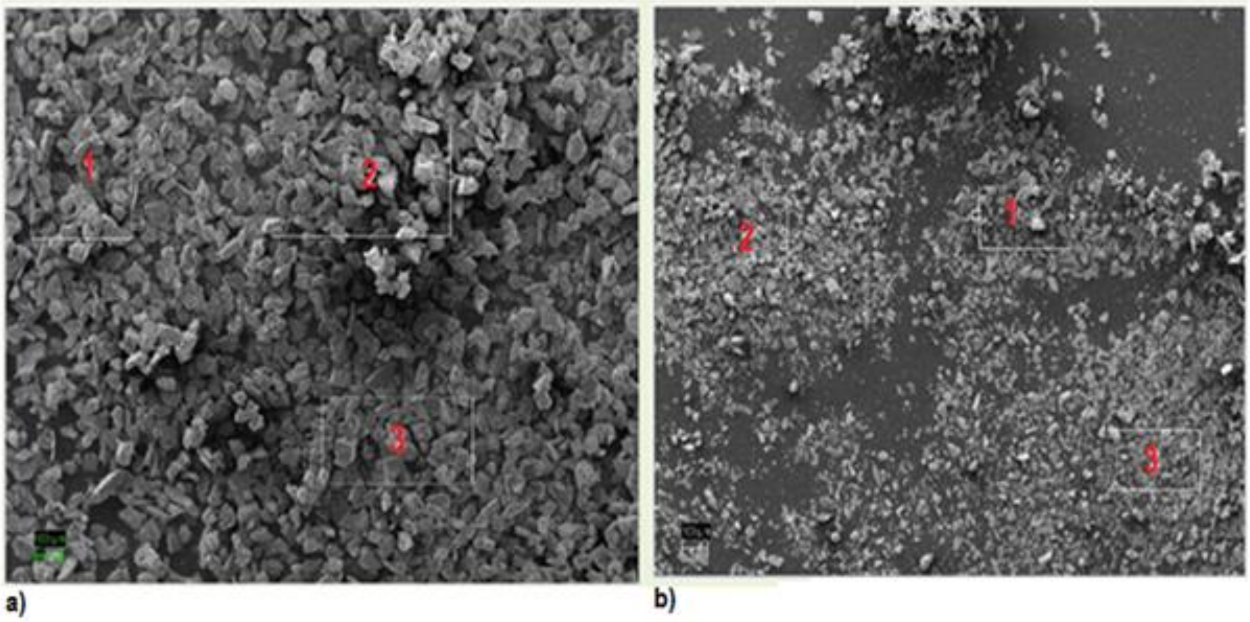
5.3.3. Fe and Mn hydroxide associated fraction

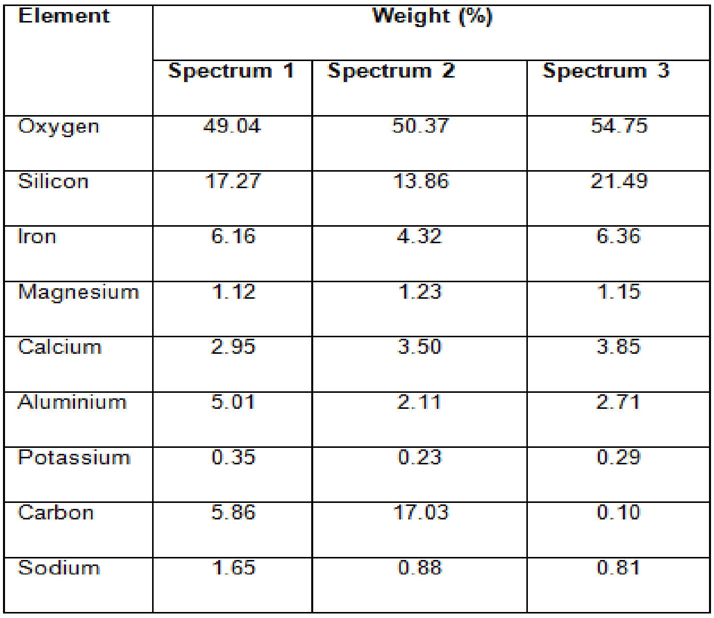
It has been reported that Fe and Mn oxides exists as nodules, concretions, cement between particles or simply as coatings on particles during mineral processing of copper, accordingly a lot of toxic elements may be pooled into this fraction when particles cool down after tailings dump disposal (Tessier *et al*. 1979; Dold, 2005). The percentage and proportion of potentially toxic or heavy metal species leached in this fraction within the respective tailings profiles followed the order: Cd (0.22-40.9 %)> Cu (19.1-32.3 %)> Pb (6.93-13.34 %)> Co (1.4-3.78 %)> Zn (2.66-3.4 %)> Mn (2.05-2.75 %)> Cr (0.63-2.14 %) (Fig.5.1). The highest proportion of Cd (40.9 %) was geochemically distributed at the upper or shallow depth (2-4 m) of tailings profile B, meanwhile the highest proportion of Cu (32.3 %) was geochemically distributed at the deeper zone or tailings- soil interface (3 m) of tailings profile C (Fig. 5.1).

The high percentage proportion of Cd, Cu and Pb in the Fe and Mn hydroxide associated fraction suggest a high affinity and fixation capacity of Fe and Mn oxides with these potentially toxic or heavy metal species in this fraction (Covelo *et al*. 2008). A fairly low leachability of Co, Zn, Mn and Cr in the Fe and Mn hydroxide associated fraction suggests adsorption and co-precipitation with the most stable oxide mineral phases such as hematite identified during mineralogical analysis (Scracek *et al*. 2010). Furthermore, Romero *et al*. (2007) corroborated that adsorption and co-precipitation of metals with oxides at near neutral pH appeared to be the mechanism controlling metal release. However, it should be noted that Fe and Mn oxides are thermodynamically unstable under anoxic conditions, as such any rapid change on the geochemical conditions of the tailings dump may result on the slow release or desorption of potentially toxic or heavy metal species locked in different physico-chemical forms in this fraction (Dold, 2005).

However, the leachable proportion major element species in the Fe and Mn hydroxide associated fraction followed the order: Mg (9.53-13.76 %)> Ca (2.68-.57 %)> Al (2.05-4.17 %)> Na^+ (0.55-1.86 %)> Fe (1.17-1.65 %). The geochemical distribution of Fe is very low in this fraction despite the high content of Fe in the tailings dump (Section 4.1.1.4.). Moreover, Figure 5.1 corroborate the low extracted concentration of major elements species such as Ca, Fe, Al, K and Na^+ in the Fe and Mn hydroxide associated fraction, suggesting they were partially released in the preceding exchangeable and carbonate fractions, respectively.

After each stage of the sequential extraction the copper tailings residue was examined using Scanning Electron Microscopy (SEM) technique. This would enable assessment of the degree of reagent selectivity and any re-precipitation associated with the extraction step. Fig. 5.3 shows the SEM images from the residues obtained after extraction of the Fe and Mn hydroxide associated fraction. The result shows that after extraction of Fe and Mn hydroxide associated fraction no obvious evidence of mineral dissolution was observed (Fig. 5.3). Calcium (precipitated as calcite) was not completely dissolved during the exchangeable and carbonate extraction stage of sequential extraction scheme as shown in the EDX result (Fig. 5.3)





Element	Weight (%)		
	Spectrum 1	Spectrum 2	Spectrum 3
Oxygen	49.04	50.37	54.75
Silicon	17.27	13.86	21.49
Iron	6.16	4.32	6.36
Magnesium	1.12	1.23	1.15
Calcium	2.95	3.50	3.85
Aluminium	5.01	2.11	2.71
Potassium	0.35	0.23	0.29
Carbon	5.86	17.03	0.10
Sodium	1.65	0.88	0.81

Fig. 5.3: Representative SEM-ED analysis under a) 100 µm magnification showing the dominant crystalline structures, and b) 10 µm magnification showing both crystalline and amorphous structures magnification validating extracted concentrations of major element species in the Fe and Mn hydroxide associated fraction.

5.3.4. Organic matter, secondary and primary sulphide fractions

The organic matter or sulphide bound fraction include metals bound to various forms of sulphide minerals and organic matter (Dold, 2003). The leachable amount of potentially toxic or heavy metal species in this fraction follows the order: Pb (0.55-57.01 %)> Cu (2.79-15.18 %)> As (0.03-11.7 %)> Mn (0.74-4.86 %)> Co (1.25-4.75

%)> Ni (0.34-4.35 %)> Zn (0.58-3.05 %) (Fig. 5.1). Despite the low content of organic matter in the tailings as indicated by the Loss On Ignition (<10 %, section 4.1.1.4, Table 4.3), the percentage proportion of Pb, Cu, and As is high in this fraction, and this fact is attributed to the soluble complexes that organic matter can form with Pb, Cu, and As.

Comparatively, the low geochemical distribution of Mn, Co, Ni, and Zn this fraction suggest that these potentially toxic or heavy metal species are strongly fixed in the organic matter fraction, thus metal immobilization (Table 5.3). Nonetheless, it must be noted that the organic matter or sulphide bound fraction is dependent on environmental conditions (Kabata-Pendias, 2010). Accordingly, under oxygen-rich conditions (i.e. high Eh) the immobilized or strongly fixed metals in this fraction may be released to the environment in the long-run when the tailings dump is in contact with infiltrating rainwater, thereby posing environmental risk with regards to receiving surface and groundwater systems. However, the percentage proportion of major element species in this fraction of the respective tailings dump follows the order: K (0.02-94.83 %)> Mg (5.71-46.82 %)> Ca (2.68-22.25 %)> Al (1.07-12.25 %)> Fe (0.02-7.17 %) (Fig.5.3). High geochemical distribution of major element species in the organic matter or sulphide bound fraction suggests a partial attack on the surfaces and corners of soluble alumino-silicate minerals that locked these major element species.

5.3.5. Residual or silicate fraction

The primary and secondary mineral-containing metals in the crystalline lattice comprise bulk of the residual fraction (Arenas-Lago *et al*., 2014). Accordingly, metals in the residual fraction are safer for the environment owing to their lowest mobility and bioavailability (Romero *et al*., 2007). To extract metals in the residual fraction the structure of the crystal lattice must be destroyed sufficiently by very strong acid or alkali solution (Dold, 2005). Nevertheless, the percentage leach of potentially toxic or heavy metal species in the residual or silicate fraction of the respective tailings profiles follows the order: Cd (20.54-99.25 %)> Cr (95.2-97 %)> Ni (91.74-97.05 %)> Zn (88.8-95.02 %)> Co (79.11-94.6 %)> As (88.29-94.5 %)> Mn (86.75-92.32 %)> Pb (33.08-87.5 %)> Cu (6.44-22.78 %) (Fig. 5.1).

The relative low geochemical distribution of Cu in this fraction suggests that much of the Cu was highly distributed on the preceding geochemical fractions or phases of the respective tailings profiles. Except for Cu, a significant percentage of potentially toxic or heavy metal species was encountered in the residual fraction. It is suggested that these potentially toxic or heavy metal species were embedded or locked in the crystal lattice structures of the primary and secondary mineral-containing them in the respective tailings profiles. Considerably, under natural environmental settings, these potentially toxic or heavy metal species will not be released into solution over reasonable time span, and therefore they are not considered as environmental risk with regards to surface and groundwater systems. This trend is in general agreement with the work done by Arenas-Lago *et al*., (2014), wherein this author established a high percentage proportion of Cr, Mn, Ni, Pb, and Zn in the residual or silicate fraction of copper tailings in Touro, NW Spain.

Nevertheless, the geochemical distribution of major element species in the residual or silicate fraction of the respective tailings profiles is shown in Figure 5.2, and follows the order: Si (99.2-99.5 %)> Fe (91.03-95.86 %)> Al (82.19-90.81 %)> Mg (26.20-45.97 %)> Ca (28.54-41.62 %)> K (5.01-9.25 %) >Na^+ (0.99-2.38 %). The high percentage proportion of Si in this fraction was inferred to the complete dissolution of crystalline quartz in which Si was embedded or locked. Similarly, the significant proportion of Fe, Al, Mg, Ca, and K in the residual or silicate fraction is attributed to the dissolution of alumino-silicate minerals under favorable geochemical conditions. The fairly low percentage distribution of Na^+ in the residual or silicate fraction suggests that much of the Na^+ was highly distributed on the preceding geochemical fractions or phases of the respective tailings profiles.

5.4. Statistical analysis

The obtained data from the seven steps sequential extraction scheme was evaluated with principal component analysis using Varimax rotation and Kaiser Normalization. Principal component analysis was applied to whole data set using SSPS V17.0 for Windows for the reduction of the obtained data in order to better understand the origin or source and the relationship between species, and the controlling factors that have the greatest influence on the retention of potentially toxic or heavy metals within the tailings by depth and tailings soil-interface. The Varimax rotated factor loadings and communalities obtained from principal component analysis for the mobile fractions are presented in Table 5.4, while the Varimax rotated factor loadings and communalities obtained from principal component analysis for the immobile fractions are presented in Table 5.5.

Table 5.4: Varimax rotated factor loadings and communalities obtained from principal component analysis for the mobile fractions.

Variables	**Comp. 1**	**Comp.2**	**Comp.3**	**Cummunalities**
Cd	0.996			1.00
Ca	0.986			1.00
Cu	-0.979			1.00
K	0.977			1.00
Fe	-0.925			1.00
Cr	-0.918			1.00
Mn	0.862			1.00
Zn		0.975		1.00
Co		0.939		1.00
Na	-0.406	0.907		1.00
Si	-0.444	0.879		1.00
Al		0.877		1.00
Ni		0.841	0.497	1.00
Mg	0.638	0.733		1.00
As	-0.686	-0.724		1.00
Pb	0.423		0.904	1.00
pH		0.541	-0.834	1.00
Total	8.012	6.747	2.241	
VAR (%)	47.132	39.687	13.181	
CVAR (%)	47.132	86.819	100	

The results of principal component analysis for the mobile fractions (water soluble fraction + exchangeable fraction + carbonate fraction) of the abandoned Musina copper tailings are shown in Table 5.4. The principal component analysis performed on the obtained data identified three components controlling the variability of the data sets in the mobile fractions. The first component amounts for 47.13% of total data variations and consists of strong loading values of Cd, Ca, K and Mn, but weak loadings of Mg and Pb. The strong loading of Ca implies the existence of this element in the tailings as calcite. This agrees with the results from the mineralogical analysis, where this element exists in the tailings in carbonate minerals such as calcite.

The second component constitutes 39.68% to the total variance and comprises positive and strong loadings of Zn, Co, Na, Si, Al, Mg and Ni. The relatively strong loadings of Si and Al were as high as 0.879 and 0.877 respectively which indicates the coexistence of Si and Al in the tailings in alumino-silicate minerals. This agreed very well with the results from the mineralogical analysis, where alumino-silicate minerals were predominant within the respective tailings profiles (Section 4.1.1.2, Table 4.2). The positive loadings of pH indicate the role the coexistence and relative mobility of these metals within the mobile fractions was also controlled by pH. The third component constitutes 13.181 to the total variance and comprises high loadings of Pb and low loadings of Ni, suggesting a different source of their origin. The positive strong loading of Pb indicates the existence of Pb in primary sulphides such as galena in the tailings, although this mineral was not identified from mineralogical analysis.

Table 5.5: Varimax rotated factor loadings and communalities obtained from principal component analysis for the immobile fractions.

Variables	**Comp.1**	**Comp. 2**	**Communalities**
As	0.997		1.000
Fe	0.991		1.000
Mn	0.988		0.989
Ni	0.979		0.984
Cu	0.955		0.975
Si	0.952		0.99
Cd	-0.946		0.993
Cr	0.945		0.999
pH	0.919		0.925
Mg	0.897		0.806
Ca	0.747	0.625	0.949
Na		0.999	1.000
Pb		0.978	0.991
K		-0.94	1.000
Al	0.5	0.853	0.977
Zn	0.655	0.743	0.982
Co	0.706	-0.706	0.997
Total	11.1	5.457	
VAR (%)	65.292	32.098	
CVAR (%)	65.292	97.39	

The results of principal component analysis for the immobile fractions (Fe and Mn hydroxide associated fraction, organic matter and sulphide fraction, and residual or silicate fraction) of the abandoned Musina copper tailings is shown in Table 5.5. The principal component analysis performed on the obtained data identified two components controlling the variability of the data sets in the immobile fractions. The first component amounts for 65.292 % of total data variations and consists of positive strong loadings of As, Fe, Mn, Ni, Cu, Si, Cr, Mg, Ca, Co and Zn, but weak loadings of Al. The strong loading values of Fe and Cu were 0.991 and 0.955 respectively, which indicate the coexistence of Fe and Cu in primary sulphides such as chalcopyrite, as identified by optical mineralogical analysis. The positive strong loadings of As, Mn, Si, Cr, Mg, Co and Zn indicated their coexistence in the silicate or residual fraction of the tailings. The positive strong loadings of pH indicate the role of pH in controlling the sorption-desorption of these elements in the Fe and Mn hydroxide associated fraction. However, the second component amounts for 32.098 % of total data variation and constitutes strong loading values of Na, Pb, Al and Zn, but weak loading value of Ca. The strong loading value of Al was 0.853 in this component, indicating the strong association of Al with the silicate or residual fraction. The weak loading value of Ca was 0.625 indicating that Ca was highly extracted in the preceding mobile fractions. Therefore, based on principal component analysis, pH and mineralogical composition of the tailings were the main substrate controlling the mobility, relationship and behavior of major and trace elements species within the mobile and immobile fractions of the tailings by depth and tailings soil-interface.

5.5. Validation of sequential extraction scheme: Element recovery

Percentage recovery of each element extracted in each fraction is important when considering the reliability of sequential extraction data. Pseudo-total digestion (total metal analysis) was performed on each sequential extraction procedure using a mixture of strong acids similarly used in the residual fraction (HF with HCl/HNO_3) as described in section 3.2.5.1. The percentage recovery was obtained by the addition of the concentrations of each metal (sum of fractions) and dividing with the total metal concentration, according to Eq.13, and results are presented in Table 5.1 for major elements species and Table 5.2 for the potentially toxic elements species.

$$\%\ \text{recovery} = \left[\frac{\sum Sequential\ extraction\ procedure}{Total\ metal\ analysis} \right] \times 100 \qquad \text{Eq.13}$$

The optimum percentage recoveries for Fe, Na and K were above 90%, and the recovery for Cu, Mn, and Ni were above 100%. The high recovery values were attributed to the possible contamination during the operation of sequential extraction procedure. However, the percentage recoveries for other trace elements such as Cd, Co and Zn were between 80-100 % indicating strong recoveries.

5.6. Summary and conclusions

The study has revealed that the mobility and environmental bioavailability of potentially toxic or heavy metal species does not only depend on the measurement of the total concentration of the metal in the solid tailings samples, but also on the chemical interactions of the tailings dump disposal with atmospheric oxygen and infiltrating rain-water (which leads to mineralogical transformation and pH variations in the tailings profiles). The following preliminary conclusions could be drawn from the study, for potentially toxic or heavy metal species in copper tailings dump disposal.

- The leachable concentration of the analytes in the water-soluble and exchangeable fractions of the respective tailings profiles was very low. The low concentration of analytes in these fractions could be due to the precipitation with secondary mineral phase (e.g. calcite) that can capture metals from the tailings pore-water systems.
- Likewise, the leachable concentration of potentially toxic element species was relatively low in the carbonate fraction of the respective tailings profiles, except for Cu and Mn which reached 10.84 mg/kg and 321.7 mg/kg, respectively at the tailings-soil interface (3 m) in tailings profile C. The high concentration of Cu and Mn suggest their high solubility, mobility and environmental bioavailability in this fraction.
- Except for Cu, Mn, and Cr, the contents of potentially toxic or heavy metal species in the Fe and Mn oxides and organic matter or sulphides bound fractions was fairly low, due to the low quantity of these fractions in the tailings, despite their high affinity and sorption capacity for potentially toxic or heavy metal species.
- Likewise, the residual fraction of the respective tailings profiles contains the highest proportion of potentially toxic or heavy metal species. Although the highest potentially toxic or heavy metal species content is in fractions with limited mobility, care must be taken since any geochemical change or shift in the tailings pH or acidic conditions may cause them to be displaced to more mobile fractions, thereby increasing their mobility and environmental bioavailability.

- Statistical evaluation showed that the extractability of the potentially toxic or heavy metal species from the seven fractions of the tailings proved to be different. The percentage recoveries for all the labile elements in the tailings samples varied from 65 % (Co) - 337 % (Mn) due to possible contamination during sequential extraction process.

CHAPTER SIX

RESULTS AND DISCUSSION 3

UNCONFINED COMPRESSIVE STRENGTH

This chapter presents experimental results obtained from the determination of the unconfined compressive strength test on three cement mix design incorporating the addition level of copper tailings by mass at C0 (0%), C5 (5%) and C10 (10%), curing at 3 and 28 days respectively. The chemical composition of the copper tailings, along with the physical properties of both the copper tailings and natural river sand, are documented. The obtained results were crucial on planning the potential beneficial application of the abandoned Musina copper tailings dump in sustaining the construction industry, as part of environmental remediation strategies for copper tailings dump disposal.

6.1. Introduction

Copper tailings are solid waste material obtained from the flotation and ore concentration stages of copper extraction process Lottermoser, (2010). The generated copper tailings are mainly disposed on landfill as tailings dump, and if abandoned may pose a threat to the surrounding ecosystems mainly through the leaching of potentially toxic or heavy metal species and sulphates occurring in a variety of minerals present within the tailings dump (Hiller *et al*., 2013). Significantly higher quantities of copper tailings are usually produced in the major copper producing countries of the world such as Chile, United States, Peru and China (Boger, 2009). According to USGS (2012), about 16 million tonnes of copper was produced across the world in 2010, and copper reserves stood at approximately 690 million tonnes. Moreover, the increasing demands for copper and copper allied products will intensify the high demands for copper. Accordingly, to satisfy these growing demands, even low grade ores with high waste volume output will be processed, owing to the billions of tonnes of copper tailings that already exists all over the world (USGS, 2012). Given the aforementioned disposal problems and potential environmental impacts associated with copper tailings, it is necessary to establish a potential planned beneficial application of copper tailings through its utilization in the construction industry as part of reuse management approach system. Nevertheless, the utilization of copper tailings dump will not only sustain the construction industry, but will also ensure job creation and minimize tailings dump environmental impacts as the disposed tailings dump will be put in good use. However, some researchers have tried to find the application of copper tailings in the construction industry with considerable success, considering the pozzolanic properties of copper tailings, i.e. high silica content, and substantial amounts of aluminium and iron. Marghussian and Maghsoodipoor (1999) investigated the blending of copper tailings with other raw materials in the production of unglazed tiles. Some studies successfully investigated the potential application of copper tailings in the manufacture of autoclaved bricks and concrete (Boger, 2009; Fang *et al*., 2011). Nevertheless, this chapter presents the results of the effect of copper tailings on the properties of cement mortar mixture (unconfined strength) containing copper tailings as an additive, as part of environmental remediation strategies for copper tailings dump disposal.

6.1.1. Physical and chemical properties of copper tailings and Natural River sand

Fig.6.1: Procured copper tailings and Natural River sand after sieve analysis.

The chemical properties or oxide analysis of the copper tailings are shown in Table 6.1, while Fig. 6.2, and Table 6.2 shows the particle size distribution and physical properties of copper tailings and Natural River sand respectively.

Table 6.1: Chemical composition or oxide analysis of the procured copper tailings (wt. %).

SiO_2	58.12
Al_2O_3	14.17
Fe_2O_3	11.7
CaO	7.5
MgO	2.6

The copper tailings contain high amount of silica and substantial amounts of iron and aluminium, which makes them pozzolanic material, and best suitable for use in cement based mix mortars. The specific gravity of copper tailings and natural river sand was 2.14 and 2.2 respectively. The relatively low specific gravity of the copper tailings was attributed to the low Fe_2O_3 content in the copper tailings. Water absorption for copper tailings and Natural River sand was 13.9 % and 9.4 %respectively. This observed trend was attributed to the prolonged exposure of copper tailings to weathering. Similar observations were made by Onuaguluchi and Eren (2012) on copper tailings at Cyprus. The observed fineness modulus of copper tailings and natural river sand was 2.77 and 4.06 respectively (Table 6.2).

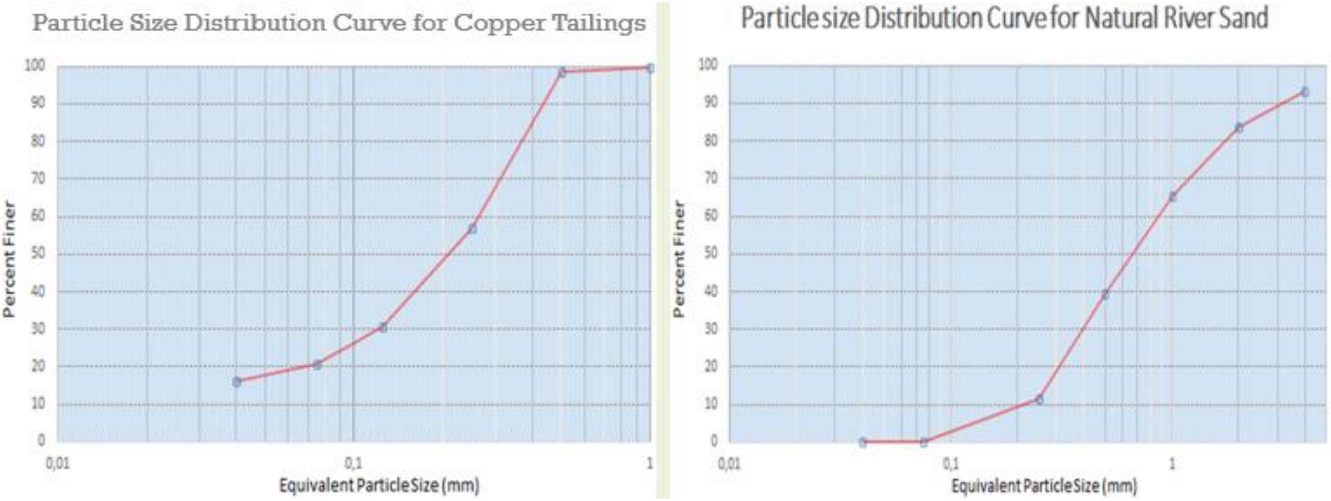
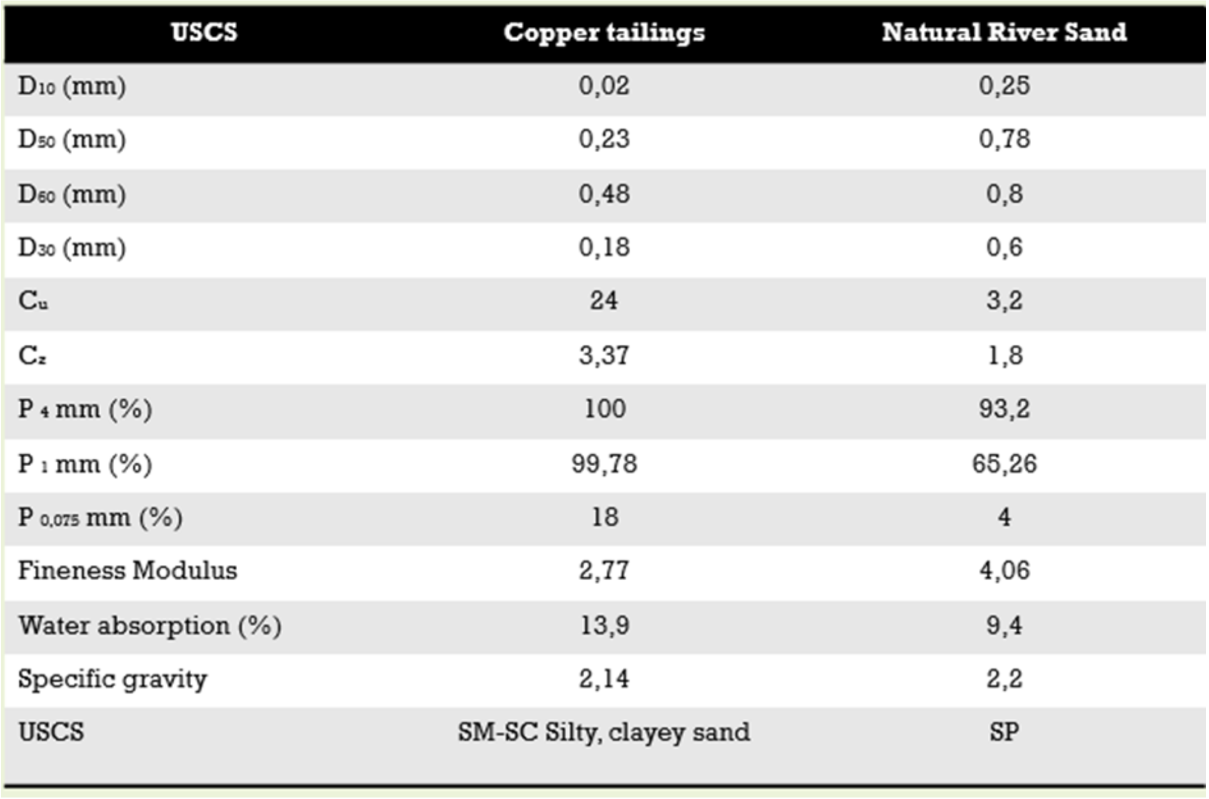


Fig. 6.2: Particle size distribution of copper tailings and Natural River sand.

From Figure 6.2 and Table 6.2, about 25 % of the copper tailings were less than 0.1mm in particle size, while the fineness was 2.77. Furthermore, with respect to Natural River sand about 6 % of river sand particles were less than 0.1 mm in particle size with the fineness of 4.06 (Fig. 6.2). The reduced fineness of the copper tailings and Natural River sand was attributed to the presence of coarse particles (75 %). Nevertheless, according to the unified soil classification scheme (USC) copper tailings were classified as silty clayey sand (i.e. sand with great deal of fines), while the Natural River sand was classified as poorly graded sand (i.e. low percentage of fines).

Table 6.2: Physical properties of the procured copper tailings and natural river sand.



USCS	Copper tailings	Natural River Sand
D_{10} (mm)	0,02	0,25
D_{50} (mm)	0,23	0,78
D_{60} (mm)	0,48	0,8
D_{30} (mm)	0,18	0,6
C_u	24	3,2
C_z	3,37	1,8
P_4 mm (%)	100	93,2
P_1 mm (%)	99,78	65,26
$P_{0,075}$ mm (%)	18	4
Fineness Modulus	2,77	4,06
Water absorption (%)	13,9	9,4
Specific gravity	2,14	2,2
USCS	SM-SC Silty, clayey sand	SP

From Table 6.2, D10 = diameter corresponding to 10% finer, D50 = diameter corresponding to 50% finer, D60 = diameter corresponding to 60% finer, D30 = diameter corresponding to 30% finer, Cu = uniformity coefficient = D60/D10, Cz = coefficient of gradation = D30 2/ (D10 D60), P4 mm (%) = percent passing sieve no. 4, P0.075 mm (%) = percent passing sieve no. 200.

6.1.2. Unconfined compressive strength

Table 6.3 shows the compressive strength results of cement mortar specimens at 3 days. The obtained compressive strength on copper tailings in Musina was compared with that observed by Onuaguluchi and Eren (2012) on copper tailings in Cyprus similarly planned to be used to sustain the construction industry. However, the results showed a slight variation at all test ages, C5 (5% tailings addition level) and C10 (10% tailings addition level) mixtures yielded higher compressive strengths relative to the control mixture (C0). The observed average compressive strengths at 3 days of casting relative to the control (C0) were 9.4 Mpa for C5 and 10.4 Mpa for C10, respectively.

Table 6.3: Obtained compressive strength of cube specimens after 3 days compared with that of copper tailings in Cyprus, C0 mixture incorporating 0% of copper tailings, C5 mixture incorporating 5% of copper tailings, and C10 mixture incorporating 10% of copper tailings by addition level.

Mixture No	**Load (K.N)**	**Avg. Load**	**Compressive strength (Mpa)**	**Avg. Compressive strength**	**Compressive strength for copper tailings in Cyprus**
C0 (0 %)	91.77 96.12 97.1	94.9	9.17 9.6 9.2	9.32	16
C5 (5 %)	95.62 94.33 92.22	94.05	9.56 9.43 9.22	9.4	14
C10 (10 %)	103.26 102.09 105.02	103.45	10.02 10.02 11.3	10.4	18

Similarly, the observed average compressive strengths relative to the control (C0) at 28 days were 26.28 Mpa for C5 and 31.15 Mpa, respectively (Table 6.4). Similar, observations were made by Onuaguluchi and Eren, (2012) when investigating the effects of copper tailings as an additive on the durability properties of cement mixture. However, it is suspected that the decreased average compressive strength on C5 at 28 days was a consequence of the water to binder (w/b ratio) and additional hydrated products such as the oil used within the inner faces of the moulds.

Table 6.4: Obtained compressive strength of cube specimens after 28 days compared with that of copper tailings in Cyprus, C0 mixture incorporating 0% of copper tailings, C5 mixture incorporating 5% of copper tailings, and C10 mixture incorporating 10% of copper tailings by addition level.

Mixture No	Load (K.N)	Avg. Load	Compressive strength (Mpa)	Avg. Compressive strength	Compressive strength for copper tailings in Cyprus
C0 (0 %)	301.37	301.2	30.13	30.4	25
	300.50		30.05		
	302.1		31.2		
C5 (5 %)	25.89	261.98	25.89	26.28	35
	264.75		26.47		
	262.3		26.5		
C10 (10 %)	311.92	311.16	31.9	31.15	37
	309.36		30.36		
	312.2		31.2		

6.2. Summary and conclusions

The high silica (SiO_2) content and substantial amounts of Fe_2O_3 and Al_2O_3, and the percentage of fines in the abandoned Musina copper tailings makes them a good pozzolana material that are moderately reactive in cement based mixtures. The addition of copper tailings at 3 and 28 days improved the compressive strength of cement mortar mixtures, although with small margin relative to the control mixture. Therefore, the potential application of these copper tailings as an additive in cement mortars in the construction industry will reduce the environmental pollution induced by the abandoned copper tailings dump disposal by putting them into good use. Moreover, this will lead to the reclamation of the land previously usurped by tailings dumps disposal.

CHAPTER SEVEN

CONCLUSIONS AND RECOMMENDATIONS

This chapter presents a general conclusion based on the main findings of the thesis, recommendations for future research and thesis output.

7.1. Conclusions

In this study, the abandoned copper tailings dump disposal situated at the eastern side of the town of Musina was investigated on two established drilled tailings profiles, with an attempt to answer the following questions governed by the objectives clearly stated in the section 1.3.

- What are the physicochemical forms and mineralogical characteristics of the tailings and how do they influence the actual mobilization of potentially toxic or heavy metal species and suitability of tailings as sustainable construction materials?
- What are the key geochemical processes that govern the partitioning and distribution of elements in various geochemical phases or fractions of the tailings dump?
- Is the metal and metalloid species bioavailable fraction in the tailings of concern to the environment, with respect to surface and groundwater resources contamination?
- Can the tailings of concern be utilized to sustain the construction industry as part of reuse approach management system to eliminate tailings dump disposal?

The following discussion will elucidate more on the success and drawbacks of the study with special regards to each of the above research questions and the recommendation for future work.

7.1.1. Physicochemical and mineralogical properties of the tailings and their influence on the actual mobilization of potentially toxic elements species within the tailings by depth

The following conclusions were drawn from the evaluation of the physicochemical forms and mineralogical properties of the tailings, and their influence on the actual mobilization of potentially toxic or heavy metal species within the tailings by depth.

- The established tailings profiles were uniform, weakly altered, and slightly varies in bulk chemical element and mineralogical composition with tailings depth. The tailings profiles have high bulk density and low air-filled porosity, with low moisture content at the upper and shallow zones of the respective tailings profiles. The tailings profiles have medium alkaline paste pH (7.97-8.37) which corresponds very well with the tailings leachates pH (8.36-8.46) and is constant throughout with tailings depth.
- The mineralogical composition within the respective tailings profiles followed the order: quartz>epidote>chlorite>muscovite>plagioclase>calcite>hematite. The alumino-silicate minerals were by far the most abundant minerals within the respective tailings profiles, along with traces of carbonates as detected as calcite (up to 3.2 wt. %). Chalcopyrite was the only primary sulphide mineral observed by optical microscopy. The high abundance of alumino-silicate minerals and traces of carbonates as calcite coupled with low sulphide mineral content suggests a high neutralization capacity of the tailings, which agreed with their medium alkaline nature. The main secondary minerals were calcite and hematite, and their proportion increased with tailings depth in the respective tailings profiles. In addition, they could retain relatively high amounts of potentially toxic or heavy metals elements (up to 862 ppm of Cu, up to 36 ppm of Ni, and up to 25 ppm of Zn) at the upper and shallow depth of the tailings, where there is high bulk density and low porosity, resulting on the low content of potentially toxic or heavy metals (up to 515 ppm of Cu, up to 14 ppm of Ni, and up to 10 ppm of Zn) in the underlying tailings and tailings soil-interface . Moreover, hematite formed coatings on the rims and corners of chlorite as observed from optical microscopy. The chemical composition of major elements within the respective tailings profiles followed the order:

Si>Al>Fe>Ca>Mg>K>Na, and corresponds very well with the mineralogical composition of the tailings, where alumino-silicate minerals were the most abundant in the respective tailings profiles. However, Al was the only major element exceeding the guideline values defined for industrial land use.

- Nevertheless, potentially toxic or heavy metals composition followed the order: Cu>Sr>Zr>Ni>Zn and their concentration were decreasing with tailings depth towards the base of the respective tailings profiles and tailings-soil interface. Nevertheless, the amounts of potentially toxic or heavy metal species released into the solution were low (0.27-0.34 µg/L Pb, 0.54-0.72 µg/L Ni, 0.88-1.80 µg/L Zn, and 20.21-47.9 µg/L Cu) decreasing with tailings depth, indicating limited mobility, and therefore, presently, the tailings have a minor impact on trace metals load transported to the receiving surface and groundwater systems. The low concentration and limited mobility of dissolved potentially toxic or heavy metal species within the tailings pore water could be due the precipitation with secondary mineral phases like calcite and hematite that can capture toxic metals from the tailings pore-water systems. The low concentration of potentially toxic or heavy metal species in the tailings pore-water were even below the drinking water limits for these elements as defined by the World Health Organization (WHO) and the South African National Standards (SANS, 2012). Based on MINTEQA2 calculation, cuprite (Cu_2O) was shown to be the most important solid phase controlling the mobility and sinking of Cu in the tailings pore water systems. Therefore, secondary minerals such as calcite, hematite and cuprite together with pH within the respective tailings profiles played an important role in the reduced dispersion of potentially toxic or heavy metal species into the receiving surface and ground water systems.

7.1.2. The geochemical partitioning and distribution, potential mobility and bioavailability of the potentially toxic or heavy metal species in different fractions or phases within the tailings and tailings soil-interface

- From the sequential extraction results, the residual fraction contains the highest proportion of the potentially toxic or heavy metal species in the order: Cd>Cr>Ni>Zn>As>Pb>Cu. Nevertheless, from the environmental point of view, the residual fraction contains silicate or primary and secondary minerals which retain high quantity of potentially toxic or heavy metal species within their crystal structure. This fraction was considered as the immobile fraction and the trace metals retained are not expected to be released into solution in the long term, and thereby moderating their severity on the receiving surface and groundwater systems.

- The leachable concentration of the analytes in the water-soluble and exchangeable fractions of the respective tailings profiles was very low. The low concentration of analytes in these fractions could be due to the precipitation of with secondary mineral phase (e.g. calcite) that can capture metals from the tailings pore-water systems under alkaline geochemical conditions. Likewise, the leachable concentration of potentially toxic element species was relatively low in the carbonate fraction of the respective tailings profiles, except for Cu and Mn which reached 10.84 mg/kg and 321.7 mg/kg, respectively at the tailings-soil interface (3 m) in tailings profile C. The high concentration of Cu and Mn suggest their high mobility and solubility in this fraction. The fraction associated with the Fe and Mn hydroxide was high in the order of Cd>Cu>Pb, indicating their high affinity for Fe and Mn hydroxide associated fraction, despite the low content of these oxides in the tailings samples.
- Except for Cu, Mn, and Cr, the content of potentially toxic or heavy metal species associated with the organic matter and secondary sulphide bound fraction was relatively low due the low content of organic matter (<10% Loss On Ignition) and the absence of secondary sulphide minerals in the tailings, despite their high affinity and sorption capacity for potentially toxic or heavy metal species.
- The proportion of major elements such as Si, Fe, and Al, was high in the silicate or residual fraction, and this high proportion was congruent with their high loading values as shown on principal component analysis in the immobile fraction, suggesting their same origin and occurrence in the alumino-silicate minerals within the residual or silicate fraction. Although, the highest content of potentially toxic element species was within fractions with limited mobility, care must be taken since any geochemical change or shift in the tailings pH or acidic conditions may cause them to be displaced to more mobile fractions, thereby increasing their mobility and environmental bioavailability. Therefore, physicochemical properties of the tailings including pH, mineralogical

composition of the tailings samples were the main substrate controlling the geochemical partitioning and distribution, potential mobility and environmental bioavailability of potentially toxic or heavy metal species by tailings depth. Nonetheless, a modified sequential extraction scheme was not applied on multiple tailings samples due to the high cost of sample analysis.

7.1.3. The potential beneficial application of tailings in the construction industry

The following conclusions were drawn from the suitability of copper tailings disposal for the development of sustainable construction material as part of reuse approach management system.

- The high silica (SiO_2) content and substantial amounts of Fe_2O_3 and Al_2O_3, and the fineness particle size of the abandoned Musina copper tailings, makes them a good pozzolana material best moderately reactive in cement based mixtures. The addition of copper tailings at 3 and 28 days successfully improved the compressive strength of cement mortar mixtures incorporating tailings at C5 (5%) and C10 (10%) respectively, although with small margin relative to the control mixture (C0). The maximum strength was 31.5 Mpa attained after 28 curing days, and slightly varies when compared with other compressive strength on copper blended cement mortars mixtures used for the development of sustainable construction materials. The chemical composition, physical properties and improved compressive strength on cement mortars mixtures incorporating copper tailings, implies that copper tailings are suitable for the development of sustainable construction materials, thereby ensuring job creation and the reduction of environmental pollution induced by the abandoned copper tailings dumps. Moreover, this will lead to the reclamation of the land previously usurped by tailings dumps disposal not only in South Africa, but also in major copper producing countries worldwide.

7.2. Recommendations

The study revealed physiochemical properties of the tailings that attenuate and control the mobility, transport and release, and potential bioavailability of potentially toxic or heavy metal species within the tailings and tailings soil-interface with respect to surface and groundwater systems, and the implication on the suitability of the tailings for the development of sustainable construction materials. Abandoned tailings dump are mainly associated with small-scale or informal mining which are often not regulated and lack good practices to ensure safety, health, and protection of the environment. To avoid the persistence discharge of potentially toxic or heavy metal species from the abandoned tailings dumps to the surrounding environment, the government should implement regulatory enforcement that will be adhered to with all forms of mining activity, whether larger or small scale mining for the protection of the environment from pollution induced by tailings dumps disposal. The study also recommends the following:

- Future work that relates to the influence of potentially toxic elements species leaching from copper tailings dumps on groundwater dynamics and its flow direction.
- Future work should also focus on the effect of other tailings such as gold tailings or cassiterite tailings on the durability properties of cement mortars containing them as additives, as part of reuse approach management system.
- Future work should also focus on the assessment of pollution induced by tailings dumps relative to the terrestrial environment (soil or vegetation).
- It is also recommended that future work focuses on improving the rehabilitation of the previously usurped land and the prevention of ingress atmospheric oxygen and percolating water at the disposed tailings dumps area.

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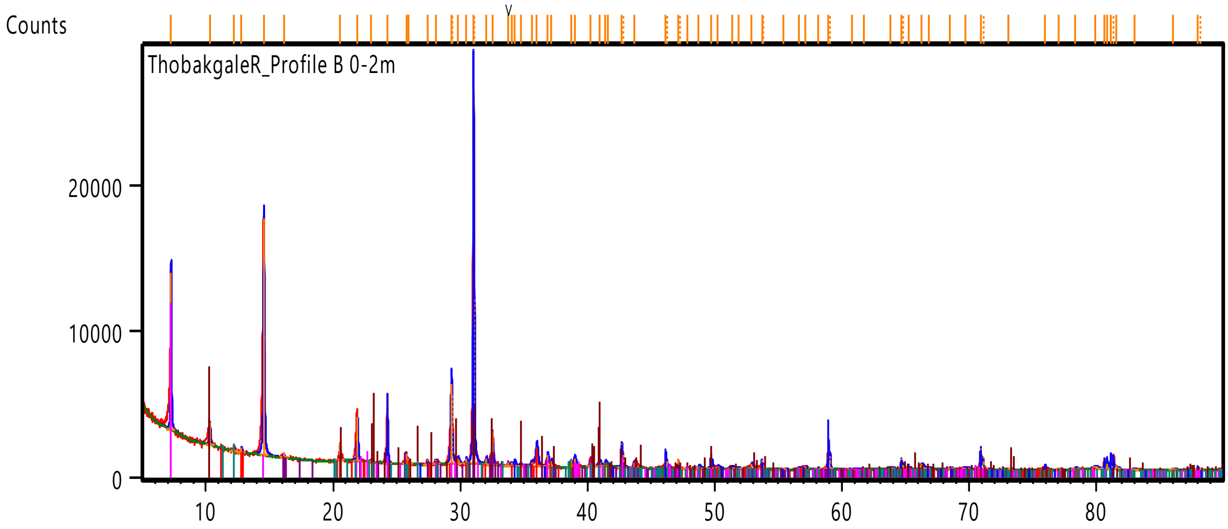
APPENDIX

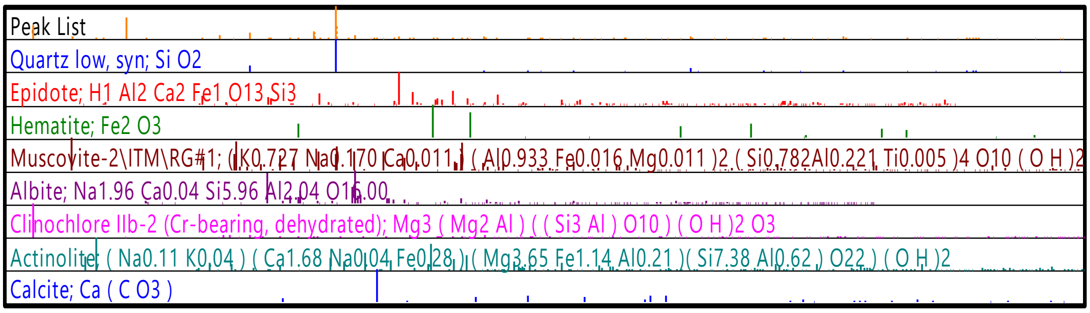
Appendix A: Physical properties of the tailings profiles

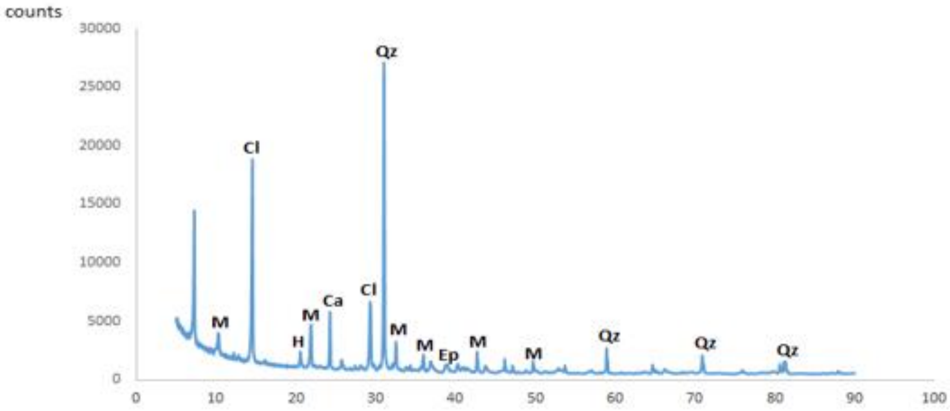
Table A1: Physical properties of the abandoned Musina copper tailings in profile C.

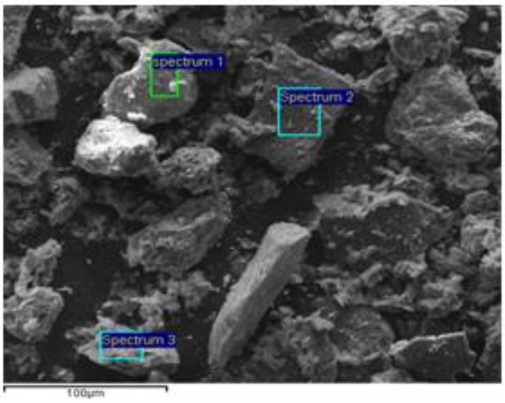
Depth (m)	Bulk density (g/ml)	Porosity (%)	Moisture (%)	Specific gravity
0-0,5	1,35	43	4,8	2,88
0,5-1	1,32	47	5,59	3,14
1-1,5	1,38	43	2,6	3,07
1,5-2	1,32	47	8,35	3,13
2-3	1,25	49	6,25	3,09

Appendix B: Mineralogical composition of the tailings profiles



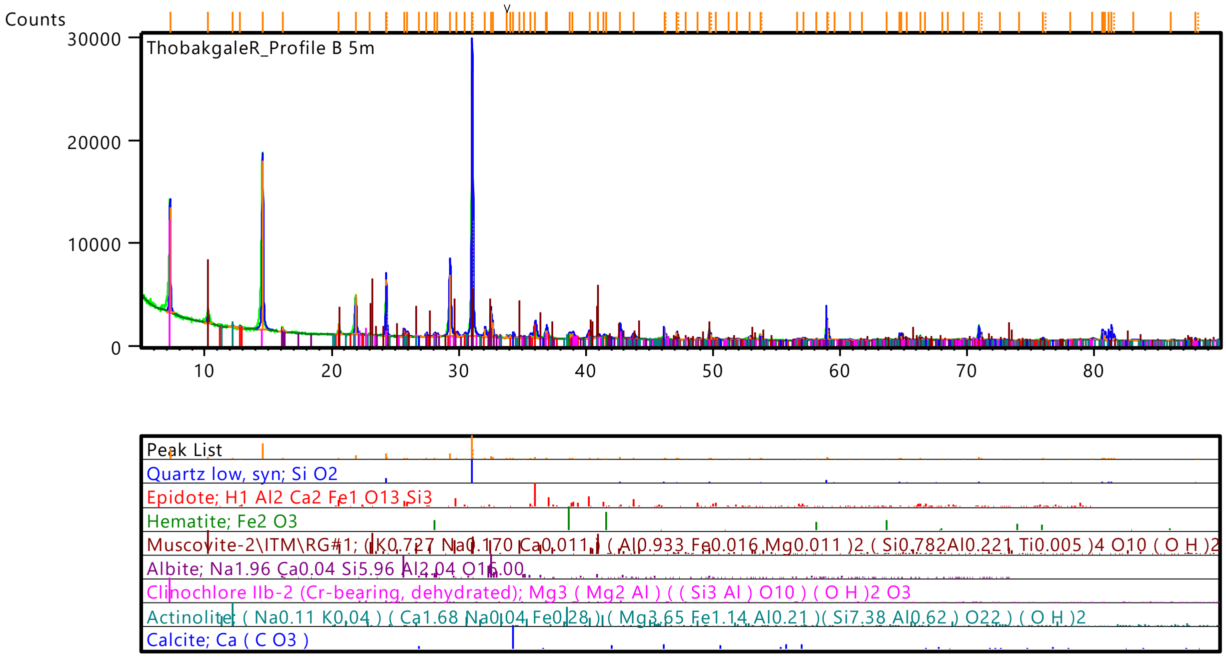


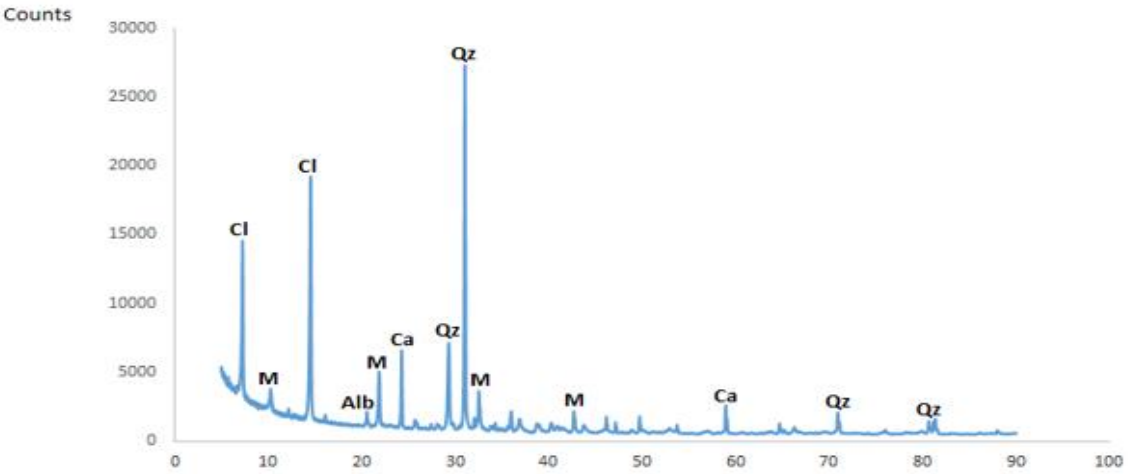


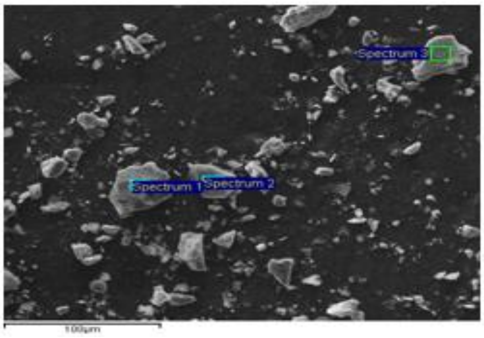


Element	Weight (%)		
	Spectrum 1	Spectrum 2	Spectrum 3
Fe	23.39	1.33	3.5
Si	13.89	38.37	26.37
Al	7.72	0.8	3.47
Mg	5.82	0.4	0.89
O	37.17	45.21	51.22
C	12.01	13.88	14.55

Fig. B 1: SEM-EDS and XRD patterns in profile B (0-2 m). Abbreviations: Qz, quartz, Cl, clinochlore, M, muscovite, H, hematite, Ep, epidote.

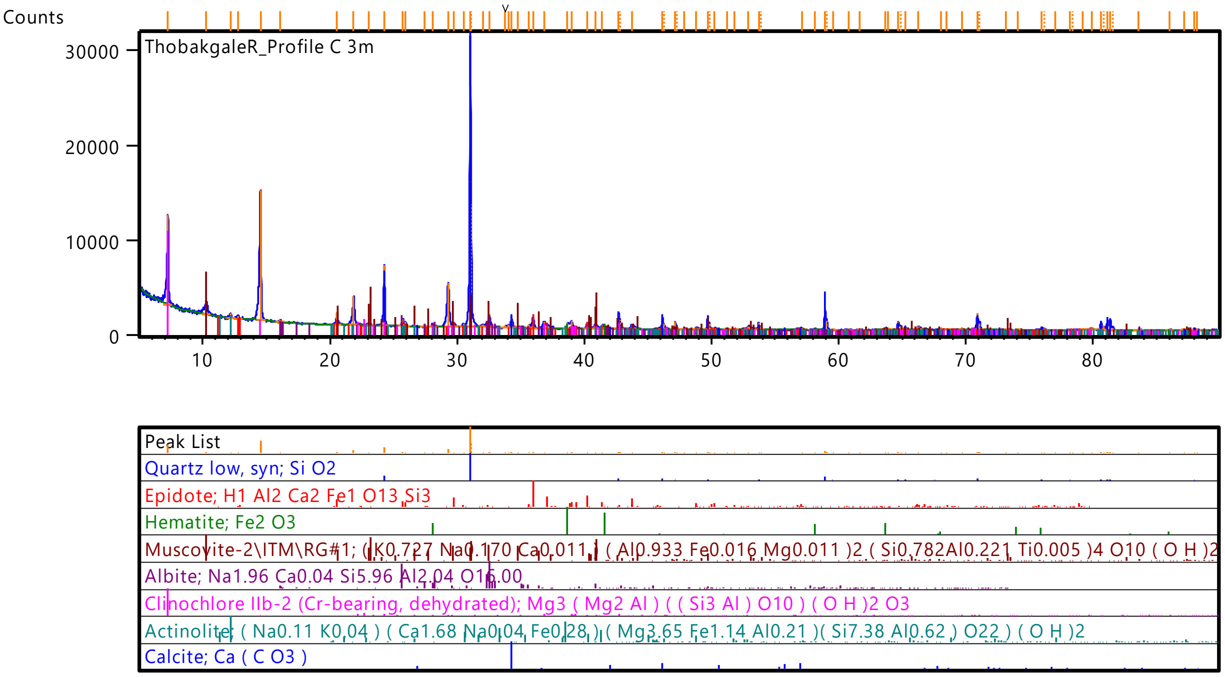


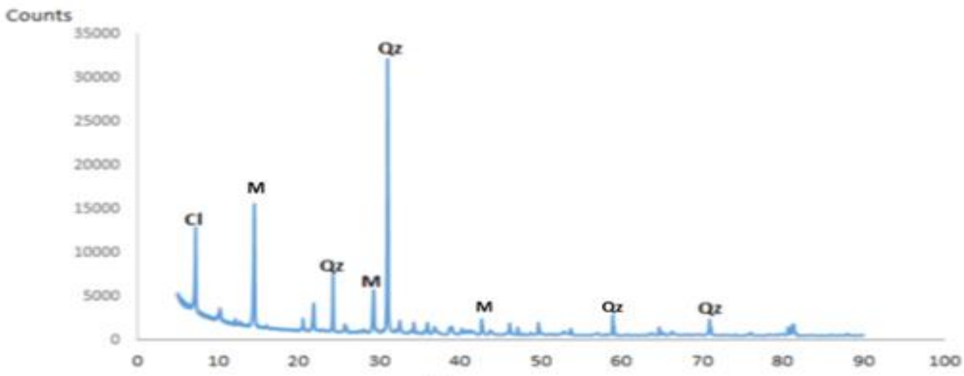


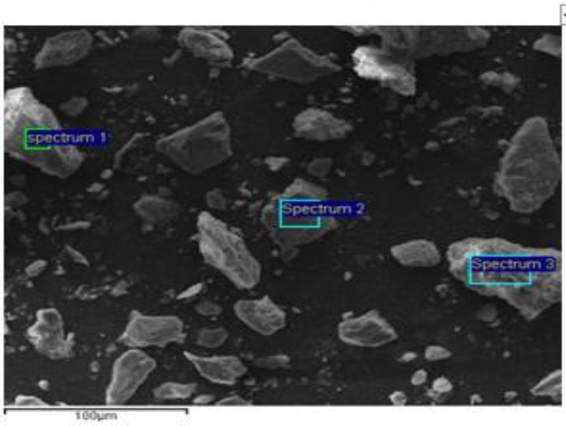


Element	Weight (%)		
	Spectrum 1	Spectrum 2	Spectrum 3
Fe	0.38	0.32	0.37
Si	35.33	40.97	36.31
O	52.59	43.29	52.45
C	11.7	15.42	10.86

Fig. B 2: SEM-EDS and XRD patterns in profile B (5 m). Abbreviations: Qz, quartz, Cl, clinochlore, M, muscovite, Alb, albite, Ca, calcite.







Element	Weight (%)		
	Spectrum 1	Spectrum 2	Spectrum 3
Fe	2.46	0.57	16.61
Si	50.8	40.62	20.34
Al	0.98	1.05	9.37
Mg	0.33	0.37	7.61
K	0.46	0.27	0.97
O	44.97	57.13	45.12

Fig. B 3: SEM-EDS and XRD patterns in tailings profile C (3 m). Abbreviations: Qz, quartz, Cl, clinochlore, M, muscovite.

Appendix C: Bulk chemical composition

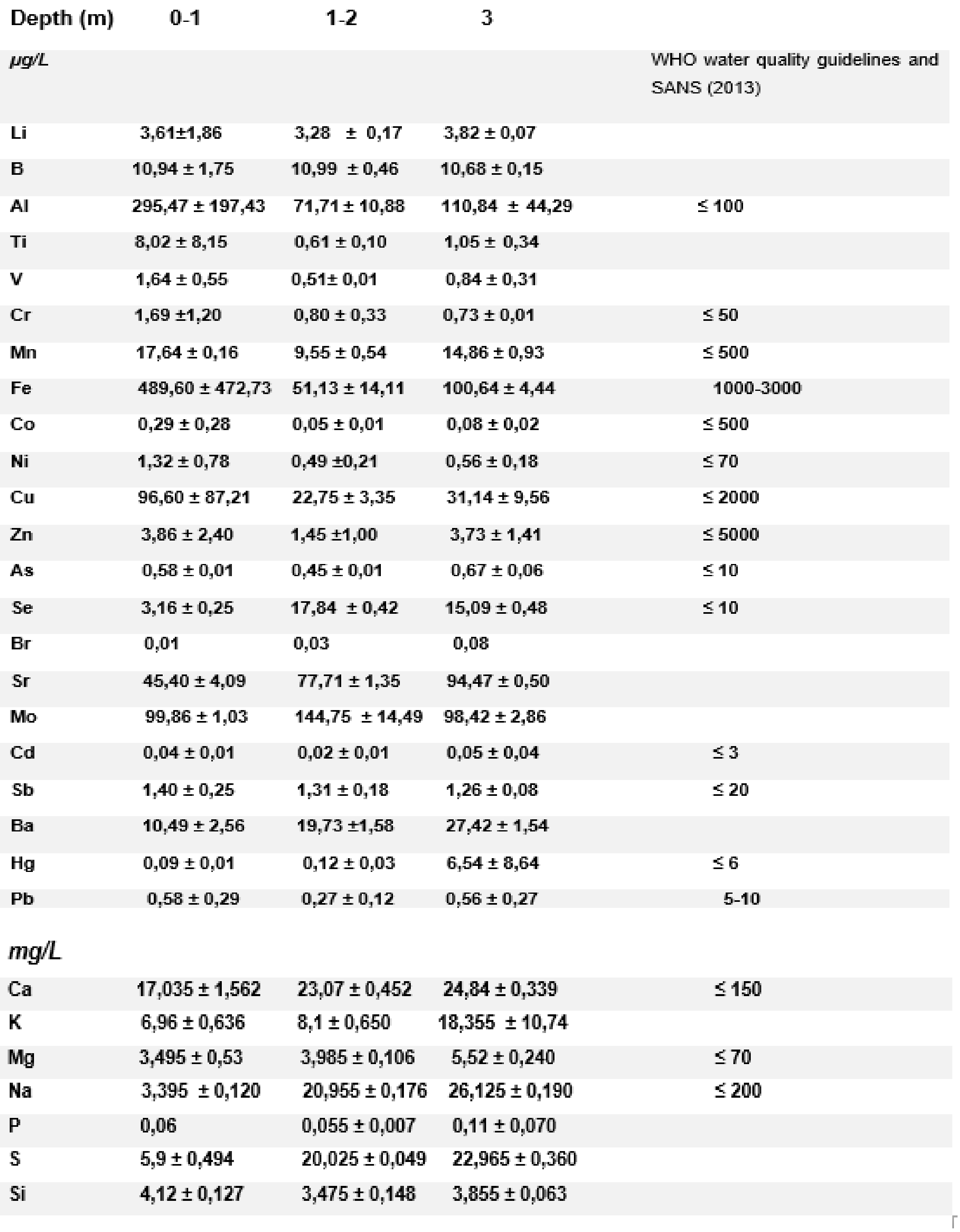
Table C 1: XRF data for major and trace elements for tailings profile C.

Paste pH	8,5	8,45	8,26	8,42	8,25
Eh (mv)	-90,8	-88,2	-77,3	-86,4	-76,6
Depth (m)	0-0,5 (top)	0,5-1 (bottom)	1-1,5 (top)	1,5-2 (bottom)	2-3
Color	Dark gray	Dark gray layer	Light/dark gray	Light gray-dark brownish	Dark gray-reddish brown
Wt.%					
LOI	3,74	3,49	3,49	3,18	3,02
SiO_2	59,49	59,48	57,25	57,30	61,14
Al_2O_3	13,21	13,55	14,13	13,23	12,63
Fe_2O_3	10,26	10,20	11,39	11,45	11,19
TiO_2	0,86	0,84	0,88	0,85	0,84
MnO	0,07	0,06	0,06	0,05	0,05
MgO	2,98	2,39	2,86	2,47	2,36
CaO	6,97	7,92	7,58	7,47	6,90
Na_2O	0,52	0,23	0,27	0,11	0,11
K_2O	0,80	0,80	0,95	0,92	0,95
NiO	0,02	0,02	0,01	0,01	0,01
ZrO_2	0,05	0,06	0,05	0,05	0,05
Total	99,36	99,41	99,33	99,46	99,58

ppm						Canadian Soil Quality Guidelines (Industrial use)
As	n.d	n.d	n.d	n.d	n.d	12
Cu	789	558	986	604	458	91
Mo	n.d	n.d	n.d	n.d	n.d	-
Ni	38	10	36	21	17	50
Pb	n.d	n.d	n.d	n.d	n.d	600
Zn	29	9	26	15	14	360
Zr	189	114	155	143	152	-
Sr	236	192	197	252	133	-
Rb	4	n.d	3	n.d	n.d	-

Appendix D: Pore water chemistry

Table C 1: Mean concentration ± standard deviation (SD) of dissolved concentrations of cations and anions from profile C.



Depth (m)	0-1	1-2	3	
µg/L				WHO water quality guidelines and SANS (2013)
Li	3,61±1,86	3,28 ± 0,17	3,82 ± 0,07	
B	10,94 ± 1,75	10,99 ± 0,46	10,68 ± 0,15	
Al	295,47 ± 197,43	71,71 ± 10,88	110,84 ± 44,29	≤ 100
Ti	8,02 ± 8,15	0,61 ± 0,10	1,05 ± 0,34	
V	1,64 ± 0,55	0,51± 0,01	0,84 ± 0,31	
Cr	1,69 ±1,20	0,80 ± 0,33	0,73 ± 0,01	≤ 50
Mn	17,64 ± 0,16	9,55 ± 0,54	14,86 ± 0,93	≤ 500
Fe	489,60 ± 472,73	51,13 ± 14,11	100,64 ± 4,44	1000-3000
Co	0,29 ± 0,28	0,05 ± 0,01	0,08 ± 0,02	≤ 500
Ni	1,32 ± 0,78	0,49 ±0,21	0,56 ± 0,18	≤ 70
Cu	96,60 ± 87,21	22,75 ± 3,35	31,14 ± 9,56	≤ 2000
Zn	3,86 ± 2,40	1,45 ±1,00	3,73 ± 1,41	≤ 5000
As	0,58 ± 0,01	0,45 ± 0,01	0,67 ± 0,06	≤ 10
Se	3,16 ± 0,25	17,84 ± 0,42	15,09 ± 0,48	≤ 10
Br	0,01	0,03	0,08	
Sr	45,40 ± 4,09	77,71 ± 1,35	94,47 ± 0,50	
Mo	99,86 ± 1,03	144,75 ± 14,49	98,42 ± 2,86	
Cd	0,04 ± 0,01	0,02 ± 0,01	0,05 ± 0,04	≤ 3
Sb	1,40 ± 0,25	1,31 ± 0,18	1,26 ± 0,08	≤ 20
Ba	10,49 ± 2,56	19,73 ±1,58	27,42 ± 1,54	
Hg	0,09 ± 0,01	0,12 ± 0,03	6,54 ± 8,64	≤ 6
Pb	0,58 ± 0,29	0,27 ± 0,12	0,56 ± 0,27	5-10
mg/L				
Ca	17,035 ± 1,562	23,07 ± 0,452	24,84 ± 0,339	≤ 150
K	6,96 ± 0,636	8,1 ± 0,650	18,355 ± 10,74	
Mg	3,495 ± 0,53	3,985 ± 0,106	5,52 ± 0,240	≤ 70
Na	3,395 ± 0,120	20,955 ± 0,176	26,125 ± 0,190	≤ 200
P	0,06	0,055 ± 0,007	0,11 ± 0,070	
S	5,9 ± 0,494	20,025 ± 0,049	22,965 ± 0,360	
Si	4,12 ± 0,127	3,475 ± 0,148	3,855 ± 0,063	

Depth (m)	**0-1**	**1-2**	**2-3**	
pH	8,46 ± 0,098	8,365 ± 0,021	8,415 ± 0,049	
EC	156,5 ± 16,829	312 ± 7,071	364 ±1,414	
TDS	18,8	18,75 ± 0,0701	18,85 ± 0,071	
ppm				WHO water quality guidelines and SANS (2013)
SO_4^{2-}	13,028 ± 3,163	47,743 ± 0,937	87,768 ± 44,631	≤ 500
Cl^-	2,106 ± 0,355	16,936 ± 0,831	24,382 ± 0,445	≤ 300
F^-	0,784 ± 0,063	1,048 ± 0,348	0,791 ± 0,022	≤ 1.5

Appendix E: Sequential extraction

Table E1: Geochemical distribution of major element species in different fractions or phases of the respective tailings.

				Chemical species (%)				
		Si	**Fe**	**Al**	**Ca**	**K**	**Mg**	**Na**
PB (2-4m)	F1	0.00	0.00	0.01	1.15	0.01	0.57	0.01
	F2	0.00	0.00	0.00	5.89	0.02	2.04	21.77
	F3	0.02	0.07	0.39	19.61	0.02	1.42	74.25
	F4	0.18	1.37	2.05	4.57	0.09	10.98	1.86
	F5	0.19	0.20	1.34	4.89	0.02	10.06	0.11
	F6	0.09	2.79	5.40	22.27	91.85	28.97	0.01
	F7	99.51	95.56	90.81	41.62	7.98	45.97	1.98
PB (5m)	F1	0.01	0.00	0.03	1.19	0.01	1.28	0.01
	F2	0.00	0.00	0.00	6.82	0.02	5.43	24.83
	F3	0.02	0.05	0.62	24.42	0.03	2.63	72.35
	F4	0.24	1.26	4.17	4.15	0.09	11.72	0.79
	F5	0.25	0.02	1.76	5.74	0.01	8.80	0.04
	F6	0.14	3.84	11.26	18.74	90.58	33.74	0.02
	F7	99.34	94.82	82.19	38.94	9.25	36.39	1.97
PC (1-2m)	F1	0.01	0.00	0.00	1.88	0.02	2.05	0.08
	F2	0.00	0.00	0.00	7.76	0.02	6.35	22.99
	F3	0.03	0.08	0.71	33.77	0.03	3.34	75.34
	F4	0.24	1.65	2.08	2.91	0.08	9.53	0.55
	F5	0.22	0.06	1.07	2.90	0.01	5.71	0.02
	F6	0.22	7.17	12.25	22.25	94.83	46.82	0.02
	F7	99.29	91.03	83.89	28.54	5.01	26.20	0.99
PC (3m)	F1	0.00	0.00	0.01	1.24	0.01	1.35	0.02
	F2	0.00	0.00	0.00	5.80	0.02	5.00	23.71
	F3	0.01	0.04	0.40	30.21	0.03	3.01	73.08
	F4	0.23	1.17	3.29	2.68	0.09	13.76	0.76
	F5	0.24	0.04	1.68	4.69	0.02	12.41	0.04
	F6	0.13	2.89	8.34	16.29	92.04	33.65	0.01
	F7	99.38	95.86	86.28	39.10	7.79	30.81	2.38

Table E2: Geochemical distribution of potentially toxic or heavy metal species in different fractions or phases of the respective tailings.

					Chemical species (%)					
		Cr	Mn	Co	Ni	Zn	As	Cd	Pb	Cu
PB (2-4m)	F1	0.00	0.01	0.01	0.01	0.01	0.02	0.00	0.00	0.04
	F2	0.00	0.06	0.09	0.04	0.00	0.04	0.00	0.01	0.15
	F3	0.17	2.20	0.85	0.21	0.00	0.00	13.56	0.17	55.15
	F4	1.15	2.63	3.78	1.36	3.40	1.79	40.95	6.93	29.49
	F5	0.59	0.95	3.58	0.47	1.00	0.03	2.22	0.55	5.93
	F6	0.94	1.82	4.62	1.32	0.58	3.85	0.00	4.88	2.79
	F7	97.05	92.32	79.11	96.61	95.02	94.50	51.92	87.51	6.44
PB (5m)	F1	0.00	0.01	0.00	0.01	0.01	0.01	29.41	0.02	0.04
	F2	0.00	0.05	0.03	0.00	0.00	0.02	29.41	0.01	0.04
	F3	0.16	2.79	0.52	0.25	3.61	0.00	8.24	0.29	42.13
	F4	1.14	2.05	1.33	0.98	3.50	1.55	14.45	13.34	27.47
	F5	0.59	0.74	1.26	0.34	1.03	1.55	0.78	1.05	5.52
	F6	1.57	2.07	2.37	1.75	3.05	4.35	4.45	19.56	6.14
	F7	96.54	92.30	94.45	96.68	88.80	92.73	20.54	65.75	18.66
PC (1-2m)	F1	0.00	0.01	0.00	0.01	0.00	0.02	0.00	0.00	0.03
	F2	0.00	0.06	0.06	0.02	0.00	0.03	0.00	0.02	0.02
	F3	0.09	5.44	1.03	0.62	1.26	0.00	0.44	1.61	48.51
	F4	0.63	2.75	1.40	2.82	2.66	1.56	0.22	8.07	19.10
	F5	0.52	0.88	1.25	0.86	0.70	0.04	0.02	0.73	4.06
	F6	3.32	4.86	4.75	4.35	1.75	11.77	0.00	57.01	10.98
	F7	95.61	86.75	92.03	91.74	93.79	88.29	99.25	33.08	17.29
PC (3m)	F1	0.00	0.01	0.00	0.00	0.00	0.02	0.00	0.00	0.03
	F2	0.00	0.04	0.03	0.00	0.00	0.02	0.00	0.02	0.12
	F3	0.02	2.96	0.35	0.17	0.63	0.00	17.70	0.28	24.29
	F4	2.14	2.35	1.37	0.99	3.88	1.18	16.25	11.77	32.35
	F5	0.73	0.74	1.45	0.39	1.19	0.03	1.02	0.63	15.18
	F6	1.72	1.62	2.21	1.40	1.22	4.44	4.92	15.39	5.75
	F7	95.24	92.26	94.60	97.05	93.05	94.29	55.35	71.86	22.28