RECOVERY AND REMEDIATION POTENTIAL OF COPPER AND OTHER PTEs IN TAILINGS FROM THE ZAMBIAN COPPERBELT

BY

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DECLARATION

This thesis is the result of the author's original research. It has been composed by the author and has not been previously submitted for examination which has led to the award of a degree.

Signed: Precious Chisala **Date: August 2022**

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DEDICATION

This thesis is fully dedicated to my mother, Justina Chitalu Chisala for believing in education and in the saying ‘‘education is the key to success’’. Mum, thank you for your sacrifices towards my career journey. I am very grateful to God for having given me you as my mother and may He bless you in abundance.

ABSTRACT

Mining activities generate large amounts of waste that can be detrimental to human health and the environment. In Zambia, mining has been ongoing since 1920 and potentially toxic elements (PTEs) have been left in mine wastes including copper mine tailings. Tailings of the Copperbelt including the bottom soil where they are currently sitting contain high enough levels of copper that they can be regarded as ore in other regions. This research focuses on recovery and remediation of copper and other PTEs in some tailings of the Copperbelt Province.

Tailings were collected from three tailings sites in the Zambian Copperbelt: Akatiti, Kitwe, and Uchi. These tailings were thought to be from different time periods of mining with Akatiti coming from the second-oldest tailings dam in Zambia and Kitwe and Uchi coming from more recent activities. Physical and chemical characterisation of the tailings were carried out. All tailings and underlying soil material were classified as coarse-grained sands with some gravel and silt present at times. All were neutral to mildly alkaline ($7.2 \leq pH \leq 8.5$). Copper content in tailings varied from 0.2-0.8% by mass, comparable to ore in other regions, and cobalt contents varied from 0.008-0.05% by mass. Underlying soils had copper and cobalt contents of 0.07-0.8% and 0.008-0.05%, respectively, indicating some mobilisation had likely occurred already. These levels indicated both opportunity for copper and cobalt recovery and need for remediation.

Copper recovery from mined materials is normally carried out by pyrometallurgical or hydrometallurgical processes. Analogous to these methods, thermal treatments and soil washing were explored for potential copper-cobalt recovery and remediation in Akatiti and Uchi tailings. Thermal treatments involved smouldering or roasting. Treating the tailings via smouldering made the PTEs become more immobile and resistant to leaching, including copper. Roasting at 600°C and 1000°C had similar effects to differing extents. Smouldering and roasting affected the mineralogy of the tailings, changing the native pH and availability of PTEs including copper to differing extents. In contrast, soil washing with 0.5 M hydrochloric acid for 24 hours recovered 94%, 100%, and 58% of copper from Akatiti, Kitwe, and Uchi tailings, respectively, while also recovering 7-45% of other PTEs. This work shows that a combined remediation and resource recovery approach is feasible for Zambia's copper tailings and should be explored to contribute to the 2030 national vision of Zambia for creating jobs for the local communities.

CONFERENCE PRESENTATIONS FROM THIS THESIS

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LIST OF ACRONYMS

AMD	Acid Mine Drainage
ASM	Artisanal & Small-scale Mining
EPA	Environmental Protection Agency
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma- Optical Emission Spectroscopy
LEAF	Leaching Environmental Assessment Framework
MDL	Minimum Detection Limit
XRD	X-ray Diffraction

1.0 CHAPTER 1 INTRODUCTION

1.1 Background

The theme of this research is the remediation of contaminated copper sulfide tailings. Mining activities generate large amounts of waste which may be harmful to human health and the environment (Boateng et al., 2012 and Coruh et al., 2013). It is estimated that more than 100 billion tonnes of solid waste are produced annually from the mining sector (Rankin, 2015). Nearly every country around the world has or had a mining industry and, thus, a legacy of mine waste. Mining waste can be classified into waste rock, tailings, slag, and temporary stockpiles (Godfrey et al, 2007). Mine wastes contain potentially toxic elements such as copper, cobalt, chromium, cadmium, lead, sulfur, and zinc which may be hazardous to human and environmental health. The problem of mining activities impacts every country with a legacy of mine waste or were mining activities are taking place. Some of the impacts of mining include deforestation and erosion (Swenson et al., 2011), contamination of streams and wetlands, dust emissions and increase in noise level (Sonter et al., 2014). Tailings are defined as, waste materials remaining after processing of pulverised ore to make a concentrate of the desired ore minerals (Ayres et al., 2003; ICOLD, 2003). Remediation strategies for mine tailings include back filling in old excavations, phytoremediation, and reprocessing, with varying successes, but further treatments are urgently needed.

In Zambia, mining activities are the core economic activities practiced in the Copperbelt region with at least four large copper mining companies active currently. These are Konkola Copper Mines (KCM), Lumwana Copper Mines, First Quantum Minerals and Mopani Copper Mines. Their mines account for 80% of Zambia’s annual copper production (Mining for Zambia, 2016). Other mines in the region include Luanshya Copper Mines and Non-Ferrous Company Africa Mining (NFCA) Plc. Zambia is thought to have more than 2.8 billion tonnes of copper reserves both explored and non-explored (World Bank, 2011). Mining is carried out by both open and underground mining. There is vast amount of copper reported as remaining in the copper tailings, enough that these materials can often be regarded as ore (Limpitlaw, 1998; Seecharan, 2013).

1.2 Environmental pollution from copper mining operations

The copper mining industry in Zambia involves the use of open pit and underground mining operations. Drilling and blasting operations are carried out. After breaking the rock to the desired size, the ore is taken to the concentrator for processing. Extraction of the copper ore is often done by a flotation process which separates the ore from the gangue (waste) at the concentrator. Copper concentrates floats to the top in the air bubbles while the waste materials sink to the bottom as tailings (Dhir et al., 2017). The tailings are removed from the flotation circuit and disposed to waste sites called tailings dams.

In the Copperbelt Province, specifically for Luanshya and Kitwe towns as well as others, tailings dams exist within the proximity of the access roads and streams because the towns have grown around copper mining. Copper tailings consists of different mineral compounds that maybe toxic to the environment and human health including aluminium, cadmium, iron, lead, zinc, oxides, hydroxides, and other compounds (Kundu et al., 2016 and Yang et al., 2013). Ore processing, including flotation, exposes these minerals to oxygen and water, making them more susceptible to weathering, formation of acid mine drainage, and pollution of their surroundings.

The mining industry is regarded as one of the major contributors of pollution to the environment and has significant impacts on human health, affecting mine workers and people living near these operations. The sector is responsible for releasing not only potentially toxic elements, nitrogen oxides and sulfur dioxides to the environment but also leaves behind a legacy of solid wastes such as tailings, and slag. Mining and ore processing is one of the environmental and occupational exposures to silica dust, asbestos, and potential toxic elements. While in the smelting processing of ore (a pyrometallurgical process), toxic gases such as SO_2 may be released, which would result in more exposure to humans and the environment (Pirrone et., 2010). Exposure to silica dust and asbestos can cause lung cancer, pneumoconiosis, and other diseases while the exposure of potentially toxic elements such as lead, cadmium and others can cause neurological and physical health effects to humans in both young and the old (Telmer and Veiga, 2009). The physical processes involved in solid waste generation from the mining industry are illustrated in Figure 1.1 below.

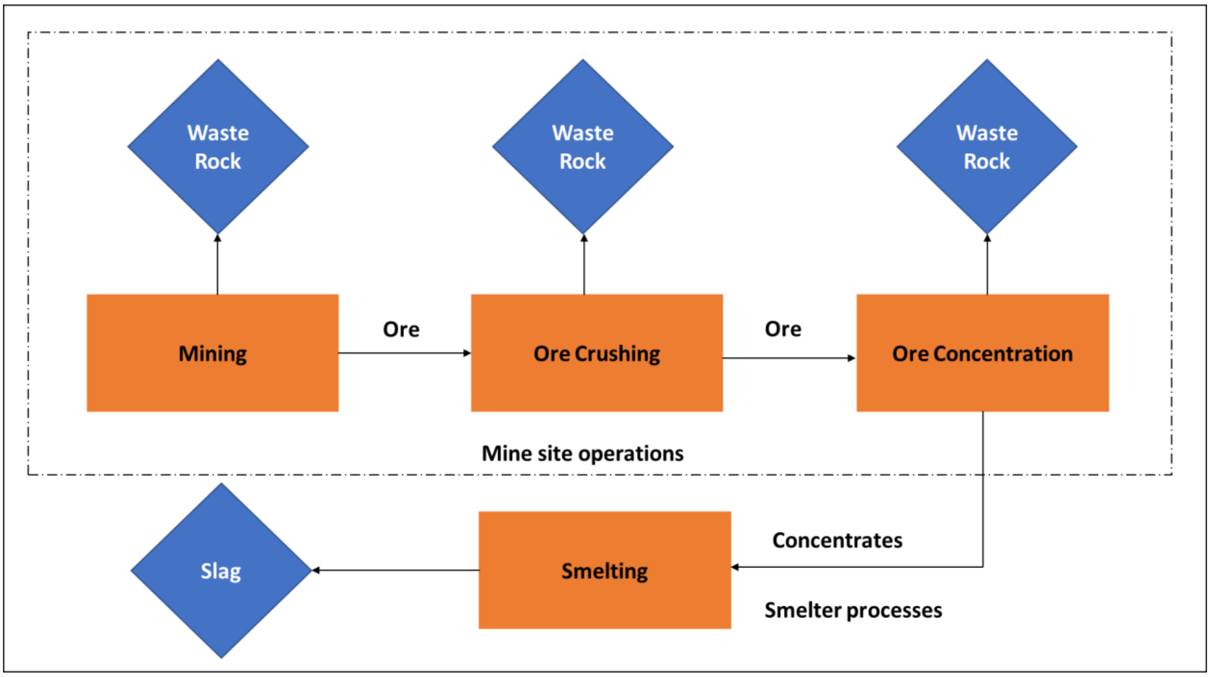

Figure 1.1 Flow diagram of physical processes involved in the generation of solid waste such as tailings and slug during mining and ore processing. (Not drawn to scale)

Copper tailings and underlying soils from the Copperbelt contain significant amounts of copper and other PTEs that pose threats to human health and the environment. This thesis explores dual aims of resource recovery of copper and other elements of potential value as well as remediation to prevent further impacts to human health and the environment.

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1.4 Scope of Thesis

This research focuses on mineral resource recovery and remediation potential of PTEs contained in the copper tailings of the Zambian Copperbelt. Tailings were collected from three sites: Akatiti tailings dam in Luanshya and Kitwe and Uchi tailings dams in Kitwe. These materials were characterised and evaluated for recovery and remediation.

1.5 Research Aim and Objectives

This thesis is aimed at investigating pollution from copper mine tailings and evaluating potential treatments for these tailings alongside recovery of valuable PTEs. The objectives of this research are:

1. Determine the key characteristics and leaching behaviour of copper tailings from the Copperbelt Region, Zambia;
2. Identify potential mineral resources (i.e., elements of value) that may be recovered as part of remediation;
3. Evaluate potential remediation methods for copper tailings and impacted soils; and
4. Develop recommendations for integrated remediation and resource recovery.

These aims and objectives were realised through a programme of experimental research and modelling.

1.6 Structure of thesis

This thesis is made up of seven chapters. Chapter 2 presents a literature review on mine waste generation from mining and mineral processing, environmental impact, and some of the existing remediation approaches. Chapter 3 presents the methodology for sample collection and preservation of samples collected from the Zambian Copperbelt. Chapter 4 presents the characterisation of the tailings and their leachability when subjected to different environmental conditions. Chapter 5 continues to investigate the leachability and treatment potential of PTEs in the tailings by roasting and smouldering. Chapter 6 presents the recovery and remediation potential of the PTEs especially copper by soil washing with hydrochloric acid. Chapter 7 presents the main conclusions and recommendations of this research and highlights research areas to be considered for future works.

2.0 CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

Mine waste is defined as the uneconomic material resulting from mining activities (Hartman and Mutmansky, 2002). Mining waste can be classified into waste rock, tailings, slag, and temporary stockpiles (Godfrey et al, 2007). The most common mineral deposits mined in Zambia are copper and cobalt. Mining in Zambia involves the use of open pit and underground mining operations, which is consistent with mining in other parts of the world. Drilling and blasting operations are carried out. After breaking the rock to the desired size, the ore is taken to the concentrator for processing. Extraction of the copper ore is often done by flotation process which separates the ore from the gangue (waste) at the concentrator. Where a flotation process is used to remove the mineral concentrate, the waste is called tailings (Dhir et al., 2017). The tailings generated from mines are usually dumped to designated mine waste dumps called tailings dams and these take up vast areas of land. Copper tailings consist of different elements and compounds which may include aluminium, cadmium, cobalt, iron, lead, zinc, oxides, hydroxides, and other compounds in addition to residual copper that may be toxic to human health and the environment (Kundu et al., 2016 and Yang et al., 2013).

As the mining industry and its employment opportunities grew in Zambia, towns grew around the mines and their tailings dams. Before mining exploitation takes place now, the company that wants to take up mining operations conducts an Environmental Impact Assessment (EIA) as per legislation of the Republic of Zambia, which was enacted in 1997. No environmental management legislation was in place before 1990 in Zambia and for this reason, limited environmental management of mine waste has taken place (Sakuwaha, 2018). The legislation did not address legacy waste. Several old tailings dams are still present in almost all mining towns in Zambia, including Luanshya, Kitwe, Mufulira, Chingola and Chililabombwe.

2.2 Environmental contamination arising from copper mine tailings

Mining activities poses potential risks of PTE contamination around the mining environment (Khameh et al., 2017). Environmental problems mainly associated with mine tailings include potential contamination of soil, water, and air (Cacciutolo and Cano, 2022). Globally, it has been estimated that more than 14 billion metric tonnes of mine tailings are produced per year from the extraction of metals and mineral forms (Global tailings review 2020). Copper tailings usually contains sulfudic components which when exposed to an oxic environment leads to the formation of oxidation processes resulting in the formation of acid mine drainage which in turn mobilises the sulfates and potential toxic elements towards the surrounding river basins and soils (Owor et al, 2006). High level impacts of tailings on the ecosystem have been caused by the dumping of the copper mine tailings into lakes and rivers or along the shore of the rivers and streams, examples include the dumping of the 500 million tonnes of copper-rich mine tailings along the shore of Lake Superior between 1850 and 1968 and this has resulted in the continuous leaching of potentially toxic elements throughout Keweenaw and the Lake Superior in Peninsula (Jeong et al., 1999). Apart from that, tailings impoundments are a concern to local communities because of dam failures and natural leaching of PTEs into groundwater and rivers (Hasen et al., 2012). Majority of PTE contamination in soils and rivers from copper mine tailings is caused by copper and to lesser extents by arsenic, cadmium, lead and zinc (Hansen et al., 1999 and Ottosen et al., 2001). The contamination of soil, water and air from mine tailings is a worldwide problem which has been studied in Chile, China, Peru, Uganda, and Iran among other nations. The studies are summarised in the table 2.1.

Table 2.1 Impact of mine tailings on the environment.

Country of study	**Type of research**
Chile	Copper, copper mine tailings and their effect on marine algae in northern Chile (Correa et al., 1999)
China	Environmental Impact Assessment of Mining Activities on Groundwater: Case Study of Copper Mine in Jiangxi Province, China (Lyu et al., 2019)
Peru	Environmental Impact Assessment of Mine Tailings Spill Considering Metallurgical Processes of Gold and Copper Mining: Case Studies in the Andean Countries of Chile and Peru (Cacciutolo and Caco, 2022)
Peninsula	Release of Copper from Mine Tailings on the Keweenaw Peninsula (Jeong, 1999)
Uganda	Impact of tailings from the Kilembe copper mining district on Lake George, Uganda (Owor et al., 2006)
Iran	Impact of tailings dam failure on spatial features of copper contamination (Mazraeh mine area, Iran) (Khamseh et al., 2017)

2.3 Impacts of mine wastes on the environment

Mine waste dumps take up vast land and some of the environmental impacts they impose on the environment include air pollution, soil contamination, water pollution and siltation, geotechnical issues, and land degradation (Lindahl, 2014). There are at least 21 waste rock dumps covering more than 388 hectares, 9 slag dumps covering 279 hectares, and more than 45 tailing dams covering an area of about 9100 hectares on the Copperbelt (Environmental Council of Zambia, 2008). In total, more than 10000 hectares of land in Zambia is covered with mineral waste. This land represents a “loss of opportunity” for the local population in terms of other land uses such as agriculture, forestry, housing, ranching, etc (SGAB et al., 2005); a loss of resources such as impacted ground and/or surfaces waters from the contamination; and potential source of harm from exposure to these contaminants.

2.3.1 Degradation of land

According to Czech Geological Survey (2007), a detailed study of soil contamination in the Copperbelt has been undertaken. The study has shown that some towns on the Copperbelt region have higher concentrations of soil contaminants resulting from mine waste disposal. Soil contamination resulting from mine tailings inhibits enzyme activity in the soil and plant growth (Kosgei et al., 2020). In the areas where these tailings are currently located, the land is affected by loss of soil fertility and potential for landslides because of lack of vegetation as shown at the Mutimpa tailings dam on the Copperbelt (Figure 2.1). The areas around the waste dumps are prone to air pollution because of the dust particles that emerge from the dry tailings during the dry season (Majer et al., 2011), which is exacerbated by the inability of vegetation to grow. The PTEs contained in the tailings are blown with this dust to nearby agriculture lands, thus affecting the fertility of the soil and potentially entering the food chain via crop uptake. When sulfide tailings are exposed to air and water, acid mine drainage may be generated, which seeps through to the ground affecting groundwater and surface water. Excess copper can be toxic (Chifungula, 2014). However, the high levels of copper contained in the tailings (Seecharan, 2013) and bottom soils may present an opportunity for copper recovery as well as a need for remediation.

Figure 2.1 Sparsely vegetated embarkments of Mutimpa Tailings Facility- KCM Nchanga exposing loose particles that can easily be blown by wind (Chifungula, 2014).

2.3.2 Water pollution and siltation

Tailings materials are deposited in designated ponds and the resulting mine drainage has a neutral to mildly alkaline pH due to liming of the tailings prior to deposition as well as high neutralisation capacity from the parent rocks (Von der Heyden and New, 2005). However, higher concentrations of copper, cobalt, nickel, and chromium have been observed in mine wastewaters on the Zambian Copperbelt resulting from mining activities (Kapungwe, 2019). In the peri urban areas, mine waste wasters are used to irrigate crops, and this has resulted in polluting the soil environment and the crops themselves because of higher levels of potentially toxic elements the wastewaters contain (Muimba-Kankolongo et al., 2021). However, higher concentrations of PTEs in the water, soil and crops from the studies indicates potential weathering of the sulfide compounds in the tailings (USDA, 2013). Higher dissolution of the sulfide compounds leads to the higher availability of the copper and other PTEs in rivers and streams (SGAB et al., 2005). In addition, various surveys in Zambia and elsewhere have shown high contamination of groundwater, soil, farm animals and wildlife, fish, rivers and streams resulting from mining activities (Owor et al., 2007; Pirrazo et al., 2010; Ettler et al., 2011; Mwitwa et al., 2012; M'kandawire et al., 2017; Muimba-Kankolongo, et al., 2021; Sracek et al., 2012).

Through leaching, mine waste can cause water pollution to the nearby water access points that are used for domestic and irrigation purposes. In the Copperbelt region, water for human consumption is received from the Upper Kafue River. Higher concentrations of dissolved elements can affect or alter the fish species and biodiversity, effects that are already noted in this river (SGAB et al., 2005). Siltation also affects the waterways in the region extensively. Siltation, or sediment pollution, occurs because of erosion from waste dumps and tailings dams, estimated at 9000 tons/year over a decade ago (SGAB et al., 2005) and likely increased since that time. A larger contribution of siltation comes from existing mining operations. For example, dewatering of Konkola Mine contributes about 15,000 tons/year of solids and the

Nchanga mining area contributes about 91,000 tons/year by discharging tailings directly into the Kafue River (SGAB et al., 2005). "Excessive siltation has a devastating impact on aquatic ecosystems and agriculture. According to the Ministry of Agriculture, farmers living near KCM's Nchanga plant suffered crop losses worth K100,300,000 during 2005 alone'' (WWI, 2019). Due to extensive siltation caused by mining activities, there is a continuous build up in the river channel and the bed sediment in many places is totally dominated by tailings material with high metal concentrations (Lindahl, 2014). This problem is not unique to Nchanga.

2.3.3 Geotechnical issues

Incidences of catastrophic damage caused by tailings dam failures have been recorded. A well-known example in Zambia is the 1970 Mufulira disaster in which 89 miners perished when the tailings above the working ground collapsed causing nearly 1 million tonnes of tailings to fill the mine workings (Davies et al, 2002). Figure 2.2 shows the aftermath of this disaster. Table 2.2 below summarises some of the fatalities recorded from tailings dam failures around the globe. Examples of geotechnical issues that are affected by tailings disposal include geology; ground and surface hydrology; and soil stability.

Figure 2.2 Sinkhole at No.3 dam burying 89 mine workers in Mufulira with the metallurgical site in the background (Nellar and Sandy, 1973).

Table 2.2 Summary of fatality accidents from tailings dam failures (Davies et al, 2002).

Date	Name	Location	Ore	Dam type	Failure Cause	Fatalities
1928	Barahona	Chile	Cu	upstream	Earthquake	54
1937	Dos Estrellas	Mexico	Au	upstream	Slope instability	70
1965	El Cobre	Chile	Cu	upstream	Earthquake	>300
1966	Mir	Bulgaria	Pb/Zn	upstream	Unknown	>10
1970	Mufulira	Zambia	Cu	-	Tailings into mine collapse	89
1974	Bafokeng	South Africa	Pt	upstream	seepage	12
1985	Stava	Italy	F	upstream	Slope instability	269
1986	Huangmeishan	China	Fe	upstream	Seepage/slope instability	19
1988	Jinduicheng	China	Mo	-	Dam breach (spillway blockage)	˜20
1993	Marsa	Peru	Au	upstream	Overtopping	6
1994	Harmony (Merriesspruit)	South Africa	Au	upstream	Overtopping/slope instability	17
1995	Sorigaodel Norte	Phillipines	Au	upstream	Foundation failure	12
		Total Fatalities				>878

Tailings dam failures are considered as one of the potential sources to cause pollution to the environment such as long-term seepage to groundwater, dust emissions and disturbance of wildlife habitats (MJRS, 1996). Examples include the Ajka tailings dam failure in Hungary (2010); Mount Polley disaster in Canada (2014); and Brazil's Mariana (2015) and Córrego do Feijão (2019) disasters.

2.4 Extraction of Copper from copper sulfide ores and waste generation

Copper exists large in two major forms: oxides and sulfides (European Copper Institute, 2021). However, most of the copper mined around the world, approximately 90%, are copper sulfide minerals such as Chalcopyrite ($CuFeS_2$) (BGS, 2007). Extraction of the copper leaves various forms of waste including overburden materials, waste rock, tailings, and slag. Copper is extracted using either hydrometallurgical or pyrometallurgy methods depending on the amount of sulfides present.

2.4.1 Hydrometallurgy

Hydrometallurgy refers to the application of solvents such as sulfuric acid to extract metals such as copper from the ore (Hocking, 2005) and are conducted at a low temperature range, up to the solvent boiling point (Francis, 2015). Leaching is one of the chemical processes under hydrometallurgy. It refers to the process of recovering metals from ores, residual material or concentrates by using aqueous solutions (Suman et al., 2019). The most common reagent used in leaching is sulfuric acid (Biswas and Davenport, 1980; Ntengwe, 2010). However, other studies have used other acids such as hydrochloric acid, acetic acid and EDTA in the recovery of non-ferrous metals such as copper and cobalt (Zhu et al., 2014). Leaching is controlled by several factors including particle size distribution, acid concentration, temperature, leaching duration and pulverisation (Ntengwe, 2010). It is also impacted by solution pH and redox (pe) conditions. The copper is extracted from the pregnant leach solution via the electrowinning process.

Tailings are produced during the froth flotation process. After mining of ore, the ore is transported and crushed into smaller rocks. This ore is then taken to the secondary crusher and ground to very fine particles. In the froth flotation process, organic wetting agents are used called collectors and frothers. For copper sulfide minerals, the common frothers used are pine oil, cresylic acid, and alcohols. Collectors, frothers and other chemical additives such as lime is added to help neutralise the pH. Water is also added in the tank to form a slurry (Ayres, Ayres and Råde, 2003). The slurry is then agitated after adding compressed air through the agitator. The bubbles of copper sulfide ore begin to form on top of the tank attaching themselves to the pine oil and the waste material sinks to the bottom. The material which sinks to the bottom is known as mine tailings (Superfund.arizona.edu, 2017). When the valuable minerals attach themselves to the air bubbles the process is called direct flotation (Wills, 2016).

2.4.2 Pyrometallurgy

Pyrometallurgy is the process of thermal treatment of metallurgical ores to cause physical and chemical transformations in the materials to recover valuable metals from them. The metal containing compounds including those of oxides and sulfides are reduced or decomposed at higher temperatures in pyrometallurgical processes (Francis, 2015). Pyrometallurgy is comprised of calcination, roasting smelting, and refining, all of which are conducted at elevated temperatures. The current technologies of pyrometallurgy uses a lot more energy than what is required theoretically (Gillett, 1996). For example, more energy is used in the process of converting sulfides to oxides via roasting and again the oxides produced may further be reduced using carbon monoxide and this process uses more energy (Ramsden, 2014). Roasting is a process that transfers valuable components from sulfides into leachable compounds. An example is the transformation of copper sulfides into acid soluble copper sulphates (Hammerschmidt, 2012).

2.4.3 Artisanal and Small-scale mining (ASM)

Small scale mining is largely an informal sector, also called artisanal mining, that includes workers that use basic tools to extract minerals from the earth (Pactworld.org, 2022). Small scale mining is one of the most important economic activities in many rural communities of Sub-Saharan Africa (Hein and Funyufunyu, 2014) and believed to play a pivotal role in poverty alleviation, contributing to national revenues and foreign exchange earnings (Hilson, 2002). However, because they are not controlled or managed, these sites are at higher risk of collapse. Also, these activities cause significant damage to the environment as they discharge potential harmful elements from the mineral processing sites or mined out areas into the surrounding soils and water bodies (Uriah et al., 2014).

In the Copperbelt, small scale mining has been undertaken at the Nkana slag dump of Kitwe commonly known as ‘‘the Black Mountain’’. The re-mining of the waste by the artisanal miners, who are locally called Jerabos, to recover copper and cobalt minerals has resulted in the loss of many lives. For example, in 2018, part of the slag dump collapsed, causing 11 fatalities (Figure 2.3) (Kapobe et al., 2019). According to the International Labour Organisation (ILO) (1999), small scale mining is expanding rapidly in developing countries and it is employing mostly women and children to work in very dangerous conditions with a fatality rate of 90 times higher than what can be experienced in industrialised companies.

Figure 2.3 Black Mountain of Kitwe and its collapse in 2018 (The Mast Newspaper, 2018).

2.5 Research background on copper recovery using electrokinetic studies of copper mine tailings as part of remediation.

Mining activities generate large amounts of waste that can be detrimental to human health and the environment (Boateng et al., 2012 and Coruh et al., 2013). Some researchers have conducted research on the removal of copper from waterly copper mine tailings using electrokinetic approach (i.e., using electric current) with a potential gradient greater than 2 V/cm. This approach has achieved 53% copper removal from the tailings using a combination of sulphuric acid to enhance the recovery process of the copper as a mineral resource with the experiment running for 21 days (Hansen et al., 2012).

In other research, the electrodialytic approach was used to achieve soil remediation of PTEs (Cu, Pb and Zn) in the tailings using the application of an electric field. Mobility of PTEs in the electric field is dependent on the dissolved phase they are in the soil. Desorption and mobilisation of most PTEs during the remediation process is activated by an acid front developing from the anode end (i.e., a negatively charged ion) of the soil (Acar and Alshawabkeh, 1993; Ottosen et., 1997). The remediation process is considered complete when the acid front reaches throughout the soil (Ottosen et., 2000). In this experiment, copper removal achieved as a means of soil remediation was 84% between 10 - 90 days. Higher removal efficiency of the copper in the electrokinetic remediation is dependent on the duration of the experiment and the pre-treatment of the tailings before remediation. Pre-treatment should be atleast 20% humidity of the tailings (Rojo and Cubillos, 2009). For example, in Rojo and Cubillos (2009) experiment on electrodialytic remediation of copper mine tailings using bipolar electrodes, removal efficiency of copper was 12 -17% using distilled water as a means of pre-treatment while 17- 25% was achieved using citric acid as pre-treatment for the same duration (18 days). Other remediation techniques that have been used to mitigate PTE pollution in soil and water from copper mine tailings are discussed further in section 2.6.

2.6 Existing remediation strategies for mine tailings

2.6.1 Back filling in open excavations

The method of back filling has been applied since the beginning of the 20th century. Examples where the method was first used include South African Gold Mines (Stradling, 1988). Because it helps in supporting the open excavations as one of the support materials, the method is still being used today in underground mines. However, the material used in back filling in underground mines varies. Sometimes waste rock or tailings are used to fill the open stopes (i.e., ground containing the ore body) to mine the adjacent ore drives or stopes. The tailings are mixed with water and cement and pumped into the mined-out areas or tunnels. The use of tailings to fill the voids helps in reducing the amount of waste that needs to be dumped on the surface by 40 – 60% (Wills and Finch, 2015), though this method can have adverse effects on ground water by leachates generated from tailings percolating through ground joints in the bedrock. Groundwater pollution in this case can be mitigated by conducting hydrogeological studies of the ground where the tailings material will be disposed of to ensure that the pit is safe enough to contain the tailings and that it will not pollute the water (Eary, 2011). Physical-chemical approaches to remediation of contaminated groundwater can be applied in these conditions, including pump and treat solutions such as reverse osmosis, air stripping or by using activated charcoal (Baier et al., 1987). However, these approaches only mitigate contamination to groundwater. Their operation must continue for as long as waste materials release contaminants.

2.6.2 Phytoremediation Vegetative Capping

Phytoremediation is a possible technique used to extract PTEs from contaminated soils using plants and is considered as an environmentally friendly remediation process. Phytoremediation is being regarded as a viable solution in treating large areas such as mine tailings and abandoned mines contaminated with potentially toxic elements. For example, the successful uptake of minerals from contaminated land using plants can be used to create recreational facilities (Karaca et al., 2016). However, it has its disadvantages such as being a longer procedure which may take a long time to achieve some degree of clean-up of the contaminated soil (Gadd, 2001). Most importantly, if PTE concentrations are too high, plants may not grow because of the toxic conditions and/or lack of microbial enzyme activity in the soil (Kosgei, 2020). Furthermore, often hyperaccumulator plants only accumulate one type of PTE on a site which is disadvantageous with sites with multiple contaminants (Lew, 2021) such as tailings dams.

2.6.3 Solidification / Stabilisation

Solidification/stabilisation is a remedial process that immobilises contaminants on site without being destroyed, degraded, or removed (Sharma and Reddy, 2004). Binding materials such as cement, clay and pozzolan are mixed with the waste to make a solid block of material trapping the contaminants and preventing them from being mobilised into the surrounding soil (Wang et al., 2015). Generally, solubilisation/stabilisation is considered a cost-effective treatment process because its additives are readily available and inexpensive and can be applied to different type of soils or waste materials (Karaca et al., 2017). However, it has shortcomings, most notably not removing contaminants from the subsurface. Other shortcomings include weight increased rate, high capacity and potential short-term stability of the concrete mix (Dermatas and Meng, 2003). Poor long-term stability may cause increased leaching of the contaminants especially if the waste to cement ratio is high. It may also lead to a reduction in the compressive strength of the concrete mix (Lombardi et al., 1998; Polettini et al., 2004).

2.6.4. Remediation and resource recovery to overcome key problems in mine tailings management

This research identified resource recovery as a key opportunity in managing PTEs in the tailings of the Copperbelt. Recovery of elements of value may offset the economic costs associated with management and remediation of tailings. Copper, cobalt, and aluminium are elements of value expected to be present in copper tailings in high concentration. Copper and cobalt are already targeted by mining operations on the Copperbelt. Further recovery from tailings would be beneficial. In addition, aluminium recovery from tailings may be advantageous because it is already in crushed form, which may save on cumminution (i.e., crushing and grinding) processes compared to mining from intact rock. Aluminium already has a growing market in Zambia. Metal Fabricators of Zambia (ZAMEFA) are currently producing 120 tonnes per month of aluminium electrical conductors and exporting to Botswana, Kenya, Malawi, Namibia, and Tanzania. Vandalism and theft of copper electrical cables have been reported by the energy supply company ZESCO Ltd (Zambia) (Kapika, 2022, The Lusaka Times), and for this reason, they propose use of aluminium cables. Aluminium cables are being considered because they are corrosive resistant, have an oxide layer, and are light weight, which prevents sagging in overhead lines (W. Mwanza 2022, personal communication, 26 March). Aluminium recovered from tailings could allow this market to grow further.

2.7 Summary of Key Findings

Copper mining started in the 1920s in the Zambian Copperbelt Province and significant quantities of copper minerals and other PTEs have been left in the mine tailings and other wastes due to inefficient processing technologies used. Mining activities can have adverse effect on human health and the environment through waste generation, water pollution, air pollution, land degradation and issues of geotechnical instability. Various treatment methods of mine tailings have been developed including backfilling, phytoremediation, and solidification/stabilisation. However, these remediation approaches have limitations, and none wholly solves the complex requirements of mining waste management. Further work is necessary to ensure safe management and remediation of mine tailings in the Zambian Copperbelt and elsewhere. Recovery of copper, cobalt, and other elements of value may present economic benefit to help offset the potentially high cost of management and remediation of mine tailings.

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3.0 CHAPTER 3 – FIELD INVESTIGATIONS AND SAMPLING

3.1 Copper mining history in Zambia

Zambia has at least 45 tailings dams in the Copperbelt region (Lindahl, 2014) developed over its near hundred-year history of copper mining. Commercial production of copper in Zambia started with Luanshya town in 1928 (Sikamo et al., 2016) and Kitwe town in 1931. Copper deposits in Copperbelt Province reach as high as 4% or more (World Bank, 2011). The tailings of the Copperbelt contain elevated levels of copper that would be regarded as ore in other regions (Limpitlaw, 1998; Seecharan, 2013). They were constructed at a time when the processing technologies were not so advanced and plant operators were not so skilled. The construction times of the older tailings dams in Zambia are not known. Some research suggests that the first Luanshya tailings dams were created in the 1950s and used from 1950s – 1980s (Basu, 2019). Copper ore deposits in Luanshya was discovered in 1902 after William Collier shot dead a Roan Antelope that died on an outcropped seam of copper which was exposed to surface along the banks of Luanshya River (Harrop, 2022). The orebody of copper in Luanshya was very close to surface depicting copper oxide ore. Three tailings dams were selected for characterisation and further experimentation: Akatiti (Old dam; 13.1375S, 28.3978E), Kitwe (TD25; 12.8591S, 28.2268E), and Uchi Lower (TD26; 12.8092S, 28.2526E). These sites were chosen for research because of reports of anticipated higher levels of copper, cobalt, and other PTEs; reports of possible washout from these tailings dams into the nearby rivers and streams (Sracek et al., 2012); and ease of access for the author.

3.2 Field visits and nature of the tailings sites

Visits to the tailings site were carried out in October 2017, August 2018, and May 2021. In the first and second visits, samples were collected for characterisation (Chapters 4-6) and the third visits included taking more photos of the sampling locations, and familiarisation of what was on the ground including looking for signs of artisanal mining since the 2017 and 2018 visits.

The tailings on the sites are sparsely vegetated (Figure 3.2) which makes them more exposed to air year-round and rainwater during the rainy season. The exposure of tailings to air and rainwater may make copper and the other PTEs more susceptible to leaching into the bottom soil and the surrounding environment. In all sites (i.e., Akatiti, Kitwe and Uchi tailing dams) there is scant vegetation covering the tailings (Figure 3.1). At the surface, the tailings look to be highly weathered. Some evidence of small-scale mining activities was noted as piles of tailings during the May 2021 site visit especially for Akatiti tailings (Figure 3.2). In 2021, the Akatiti tailings dam had fencing around it that was not present in 2017 or 2018.

Figure 3.1 Wider view of the degraded Kitwe tailings dam sparsely covered with trees or grass (May 2021).

Figure 3.2 Small pile of tailings excavated from the front wall of the Akatiti tailings dam suggests activity of artisanal miners (May 2021).

White precipitate was visible on some of the Akatiti and Kitwe tailings (Figures 3.1 and 3.3), which suggests some mobilisation of PTEs from the tailings into their surroundings.

Figure 3.3 Close view of Kitwe tailings dam and white precipitate present on exposed surfaces (May 2021).

3.3 Sample collection and preservation

Samples were collected using a hand auger at the three sites (Akatiti, Kitwe and Uchi tailings dams). Tailings samples were obtained by drilling horizontal holes through the tailings up to 135 cm (Figure 3.4) while the underlying bottom materials where the tailings are sitting were obtained by drilling vertical holes up to 15 cm from top surface (Figure 3.5). At all sites, tailings and underlying soil used in the analysis were collected from the sidewall of the copper mine tailings facing the easily accessible routes. Samples were collected at 1 m intervals along a 25 m sampling line (Appendix A), The samples were stored in polythene bags and sent to the UK for study. Upon arrival they were stored at 4°C.

All samples were air dried to determine moisture content following BS ISO 11464: 1994 prior to further testing. pH was measured following BS ISO 10390:2005. Soil classification (particle size distribution) of the materials was done following BS ISO 11277:2009. Total carbon was determined by heating the material at 550 °C in a muffle furnace for 4 hours and cooling to ambient temperature (BS ISO 15169: 2007). All measurements were conducted in triplicate.

Figure 3.4 Sampling through the tailings by drilling horizontally using a hand auger.

Figure 3.5 An illustration of vertical sampling of underlying soil materials using a hand auger. The hand auger was drilled by twisting it in a clockwise direction to reach the desired depth for bottom soil sampling.

3.4 pH dependence test (Method 1313)

Method 1313 is a parallel batch extraction test that consists of 9 test positions with pH values ranging from $2 \leq pH \leq 13$. The pH of the test positions is varied using nitric acid and potassium hydroxide. The extraction bottles containing the solid material and acid/base solution are tumbled end-over-end for a specified contact time based on the particle size of the solid material to be tested. A liquid-solid partitioning curve is produced for a particular pollutant of interest by plotting its available concentration against the pH range (US EPA, 2012). Available content is defined as the maximum release (mg/kg) of a constituent over the full domain of the

Method 1313 test results. The available content at a specific pH value gives an estimate of a practical value of potential release of constituents into the environment that maybe used as a bounding estimate concentration (US EPA, 2019). The liquid-solid ratio of 10 mg/L-dry is maintained in all 9 sample positions in this pH range.

There are four characteristic leaching behaviours exhibited by the pH static test, namely amphoteric, cationic, highly soluble, and oxyanionic behaviours (Figure 3.6). Amphoteric behaviour is when PTEs tend to have a higher concentration in the acid region, release a minimum concentration in the near neutral pH range, and increase in concentration again in strong alkaline conditions. Cationic leaching behaviour is achieved when a material releases higher concentrations of PTEs of concern in acidic conditions, but concentrations decrease in the neutral to alkaline range. Highly soluble behaviour is PTEs of concern when PTE concentrations do not depend on the pH variation, and they may leach to the point of depletion. Finally, oxyanionic behaviour is when the PTEs show a maximum release in the neutral to slightly alkaline pH range and concentration is decreased when pH decreases into the acidic range (pH < 7) or increases into the strong alkaline conditions (pH > 10) (US EPA, 2019). These four characteristic profiles (Figure 3.6) provide basic evaluation of how PTEs may behave in complex natural systems (US EPA, 2017)

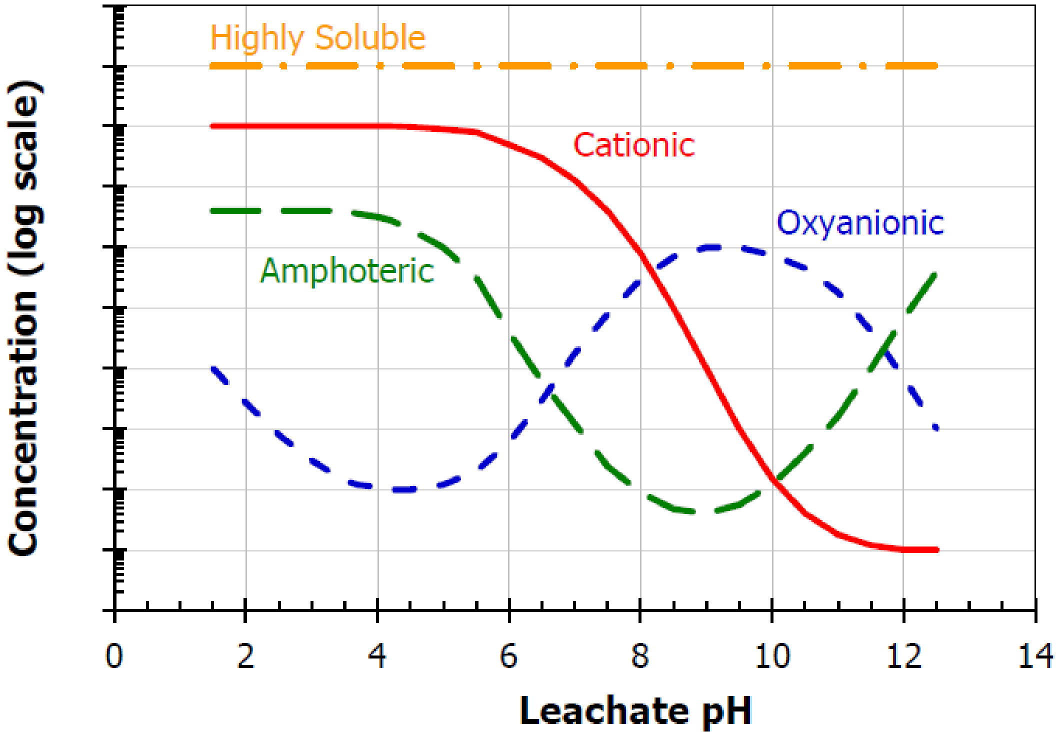

Figure 3.6 Classical leaching patterns of the pH dependent leaching test adapted from Kosson et al., (2002) as cited in U.S. EPA (2012).

3.5 Percolation column leaching (Method 1314)

The percolation column leaching experiment is used to obtain the eluate concentration or cumulative release of a particular constituents of potential concern using the natural pH of the material and is plotted as a function of the liquid-solid ratio (L/S) (US EPA, 2013). The column is packed with a granular material and the eluent is passed through the column using an up-flow pumping method to avoid air entrapment and flow channelling. The most common eluent used is deionised water but sometimes 1 mM of calcium chloride is added for materials containing a lot of clay to avoid deflocculation (Garrabrants et al., 2010). Nine aliquots of varying volumes of up to 10 mL/g dry sample are collected and analysed for eluate concentration and a cumulative release for the potentially toxic elements of interest. An illustration of the experimental setup for a column leaching experiment is shown in figure 3.7.

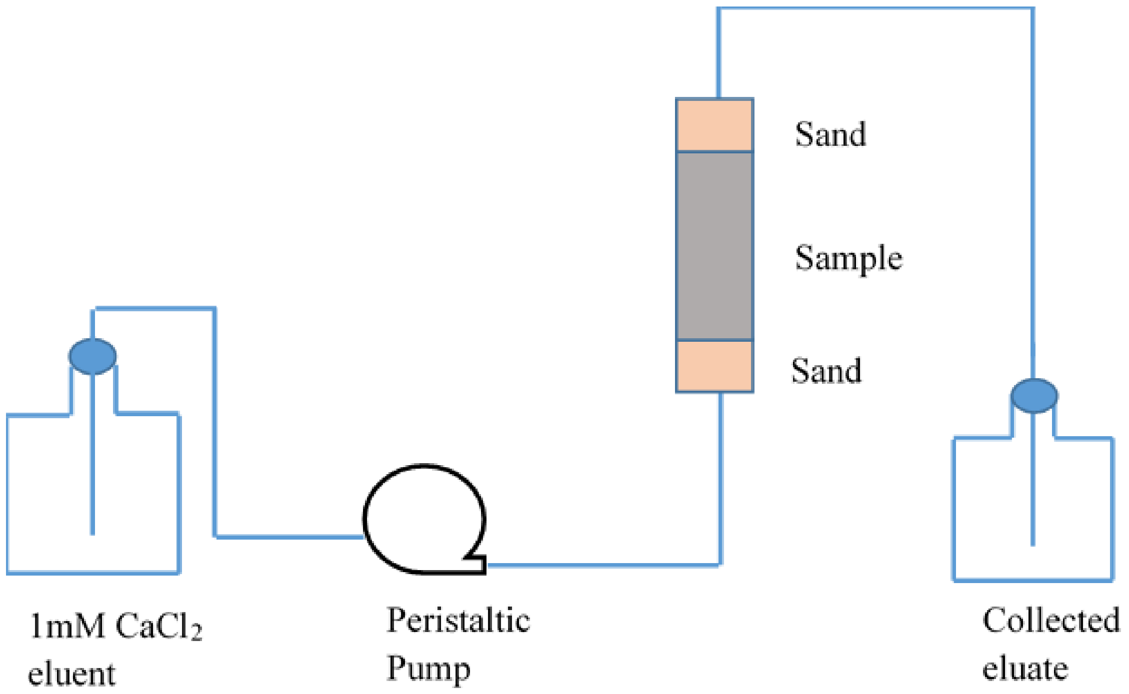

Figure 3.7 Schematic diagram of column leaching setup for US EPA Method 1314 (not to scale).

Eluate concentrations from the Method 1314 test positions may be used along with Method 1313 liquid-solid partitioning over $2 \leq pH \leq 13$ and geochemical speciation modelling to identify the mineral phases and partitioning processes that control the Liquid-Solid Partitioning in the pore structure of the solid material (van der Sloot and Kosson 2007; van der Sloot et al. 2008).

In this research, pH dependent availability (Method 1313) and column leaching (Method 1314) were used as part of the environmental leaching assessment to evaluate the potential release of PTEs from the copper mine tailings and underlying soils as well as to evaluate remediation methods (Chapters 4 – 6).

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4.0 CHAPTER 4 – COPPER AVAILABILITY AND MOBILITY FROM HISTORIC TAILINGS SITES IN ZAMBIA.

ABSTRACT

Mining activities generate large amounts of waste that can be detrimental to human health and the environment. The history of copper mining in Zambia dates to the 1920s and, from its inception, nearly 800 million tonnes of copper mine tailings have been created country wide, impacting about 10,000 hectares of land. Exposed tailings risk releasing potentially toxic elements into ground and surface water. Tailings and soil samples were collected from three locations: Akatiti (Old dam), Kitwe (TD 25) and Uchi Lower (TD 26) tailings dams. Among these locations, Akatiti is thought to be the second oldest tailings dam in Zambia while Kitwe and Uchi were built more recently. Potentially toxic element (PTE) leachability was characterised using pH dependence and column leaching tests from the USEPA Leaching Environmental Assessment Framework. Based on total and available contents, copper and cobalt were identified as in need of remediation but also opportunities for resource recovery in the tailings and, in some cases, bottom soils. Higher content and availability of PTEs from some bottom soils, particularly copper, shows that PTEs have likely leached from tailings into the surrounding soils, potentially affecting ground and surface water. At pH ≤ 4, the amount of copper extracted using the pH dependence test was approximately, 83% for Akatiti, 73% for Kitwe and 43% for Uchi tailings indicating a good potential for recovery from some tailings via hydrometallurgical extraction methods.

Keywords: mine tailings, copper, potentially toxic elements, leaching, resource recovery

4.1 INTRODUCTION

The history of mining in Zambia dates to the early 1920s (Sikamo, et al., 2017). From the inception of mining activities, significant amounts of mine waste have been generated in the country. A report in 2005 estimated that there were 77 million tonnes of waste rock and 791 million tonnes of mine tailings in Zambia (Sikaundi, 2005). Annual production of copper has more than doubled since that estimate (Mfula, 2020). There are at least 45 tailings dam on the Zambian Copperbelt covering 9125 hectares of land (Lindahl, 2014).

In 1993, 38 million tonnes of solid waste were produced annually, and mine tailings accounted for about 90% of this figure (Banda and Zulu, 1993). Since 1993, mining operations have increased and this is evidenced by the opening of new mining operations such as Kansanshi copper and gold mine (2004) in Solwezi, Lumwana copper and gold mine (2008), Kalumbila copper and gold mine (2010); and Muliashi open pit mine in Luanshya (2013).

Mining is carried out by open pit and underground mining operations. Open pit mining is practiced in cases when the orebody is closer to surface and when the grade is low (below 0.5%) while underground mining is practiced when the orebody is deep and with high grade (1-2%) (Calcutt, 2001; Davenport et al., 2002). The average grade of copper on the Zambian Copperbelt is around 3% (Bowen and Gunatilaka, 1933; Kamona and Nyambe, 2002 cited in Křibek, 2011).

Mining of copper from the earth crust involves drilling and blasting operations. The loose rocks are crushed and ground or milled into fine particles so that the ore can easily be separated from the waste rock. Copper is then extracted via the hydrometallurgy route for copper oxides or pyrometallurgy route for copper sulfides. Extraction of copper using hydrometallurgical processes involves the use of dilute sulfuric acid (Hocking, 2006) for direct acid leaching while pyrometallurgical processes consists of roasting and smelting (Mishra, 2001) to concentrate copper and drive off impurities. Both approaches are used in Zambia.

Tailings are waste materials generated during ore processing by crushing, grinding, and concentrating copper (Ayres et al., 2003; ICOLD, 2003; Geng et al., 2017). On the Copperbelt, tailings dams were constructed using a downstream method where new lifts were added, and embankments increased in height downstream so that tailings constructions remain geotechnically stable as they increase in size. The physical properties and nature of tailings depend on the parent rock and copper extraction processes (Lottermoser, 2010). Copper mining waste contains residual copper as well as other potentially toxic elements (PTEs) (Boateng et al., 2012; Çoruh et al., 2013; Hossner and Hons, 1992, Mendez and Maier, 2008) that may be susceptible to leaching and mobilisation into surrounding soils, groundwater, and surface water (Al-Jabri et al., 2006; Angelovičová and Fazekašová, 2014; Marguí et al., 2004). The aims of this research were to characterise representative tailings and underlying soils of the Copperbelt region and assess the risks of PTE mobility from them to the surrounding environment. These aims were achieved through a programme of experimental work using the USEPA's Leaching Environmental Assessment Framework (LEAF) protocols (EPA, 2017).

4.2 METHODOLOGY

4.2.1 Geology and Geography of the Copperbelt Region of Zambia

The geology of the parent rocks is part of the general geology of the Copperbelt region characterised in the *Katanga Super-Group*. The geological formation in the Katanga region consists of argillaceous and carbonate shale, dolomite, and limestone (Binda, 1994 and Rainaud et al., 2005). Copper cobalt iron sulfide is the most dominant ore in the Copperbelt. It is mainly composed of bornite ($CuFeS_4$), chalcopyrite ($CuFeS_2$), carrolite ($Cu (Co,Ni)_2 S_4$) and pyrite (FeS_2) (Ondra et al., 2011). Other mineral phases integrated in the ore formation are dolomite, quartzite, and shale (Mendelsohn, 1961). However, acid soluble copper oxides including cuprite, malachite, azurite, and tenorite are also integrated in the ore formation

(Habashi; 1997, Hayes, 1985 and Shabani et al., 2012). Copper and cobalt have average grades of 3 % and 0.18 %, respectively, in the orebody (Bowen and Gunatilaka, 1933; Kamona and Nyambe, 2002 cited in Křibek, 2011).

The population of the Copperbelt is around 2.6 million people (Zambia Statistics Agency, 2021). The mining industry has employed more than 90,000 people with direct jobs (Sikamo et al., 2016) and more in indirect or supporting industries. Copper accounts for 10% of Zambia's GDP and nearly 80% of its exports (Sikamo et al., 2016). Copperbelt Province experiences three climatic seasons: a rainy season from November to April (20.6-23.6°C), a cold-dry season from May to July (17.9-20°C), and a hot-dry season from August to October (20-25.7°C). Average annual temperature is 20°C and average rainfall per year is 1200 mm with much of it concentrated in the rainy season. Mining and disposal activities are carried out year-round. Discharge of rainfall into local streams is highly variable between the dry and rainy seasons with most precipitation discharged into rivers and streams during the rainy season (Petterson and Ingri 2001). These seasonal differences likely affect PTE mobility from tailings.

Mine waste occupies <1% of the land area of the Zambian Copperbelt; however, waste disposal sites are disproportionately concentrated around population centres, reflecting the development of the mining sector locally and population growth around employment opportunities. This waste presents a loss of opportunity for the local people to use the land for other ventures such as such as housing, ranching, agriculture, and other activities (SGAB et al. 2005). Proximity of mining activities and waste disposal sites to local populations affects air quality, drinking water quality, irrigation water quality, and agriculture. Runoff water from mine tailings containing PTEs can seep into nearby streams or rivers (Peša, 2020). Dust particles containing PTEs can be mobilised by wind causing air pollution, especially in the dry seasons (Kosgei, 2020). Because of inefficient extraction processes, copper content in waste tailings is relatively high and informal re-mining of waste tailings exacerbates existing health and environmental problems. Because of the extreme differences in precipitation between wet and dry seasons, tailings may vary from being completely saturated by rainwater to complete exposure in air throughout a typical year.

4.2.2 Akatiti, Kitwe, and Uchi site descriptions

Tailings and soils were sampled from Akatiti (TD Old dam; 13.1375S, 28.3978E), Kitwe (TD25; 12.8591S, 28.2268E) and Uchi Lower (TD26; 12.8092S, 28.2526E) tailings dams in Luanshya and Kitwe, Zambia (Figure 1-A, supplementary materials). Copper deposits in Luanshya were first identified in 1902 by a prospector/explorer named William Collier after he shot a Roan Antelope along the banks of the Luanshya River and discovered an outcrop of copper ore (Harrop, 2022). Commercial production of copper in Zambia started with Roan Consolidated Copper Mine in Luanshya in 1928 and in Kitwe in 1931 (Sikamo et al., 2016).

Akatiti tailings dam is one of the three tailings' dams in Luanshya and the second to be constructed. It is located in the north of Luanshya town and surrounded by development on all sides. Akatiti tailings dam occupies a land area of 240.4 hectares, has an average height of 30 m, and contains approximately 45 M tonnes of waste tailings (Sakuwaha, 2018).

Kitwe (TD 25) and Uchi Lower (TD 26) tailings dams are both in the centre of Kitwe reflecting the town's growth around mining activities. The complex of the mine incorporated a smelting plant, a refinery, sulfuric acid production facility, concentrators, and cobalt plants as metallurgical plants. Kitwe and Uchi dams are among 18 tailings dams in and around Kitwe but only Mindola West (TD15A), west of Kitwe town, is still operational. Tailings dams in Kitwe town occupy 1500 hectares of land and contain more than 250 million tonnes of tailings (Huderek, 2009). Kitwe tailings dam occupies 111 hectares and contains approximately 27 M tonnes of waste tailings (Muleya et al, 2020). Uchi Lower tailings dam and its partner site Uchi Upper occupy a land area of 100 hectares. Uchi Lower is the smaller of the two sites and contains approximately 8.4 M tonnes of waste tailings.

The Dutch screening values guided in Esdat (2009) were used to identify PTEs of potential concern in the tailings and their respective underlying bottom materials. Tailings dams were visited between October 2017 and August 2018 during the dry season. No standing water was observed.

4.2.3 Sample collection and preparation

Tailings and soil samples were collected using a hand auger. Samples were collected from the side wall of the tailings along the access routes. Tailings were obtained by drilling horizontally to 135 cm. Underlying materials (called “soils” here but may be older tailings) by drilling vertically to 15 cm. Samples were collected from the sidewall facing the access routes at 1 m increments along a 25 m sampling line. Approximately 25 kg of tailings and underlying soil were collected at each site. The samples were stored in polythene bags, transferred to Glasgow, UK, air dried following BS ISO 11464: 1994, and homogenised before further testing. pH of the tailings and soils was measured following BS ISO 10390:2005. Soil classification was determined following BS ISO 11277:2009. Total carbon content of the materials was determined by heating the material at 550 °C in a muffle furnace for 4 hours and cooling to ambient temperature (BS ISO 15169: 2007). All measurements were conducted in triplicate.

4.2.4 Characterisation of total copper and other elements

Pseudo-total contents of Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Na, Ni, P, Pb, S and Zn were determined. Samples of approximately 0.4 g were digested in triplicates of 10 mL acid volume with a ratio of 1:4 (i.e., 2 ml HCl and 8 ml of HNO_3) using an NF grade concentrated hydrochloric acid (33%) and an ACS grade nitric acid (67%) in a MARS Xpress (CEM Corporation) following USEPA Methods 3051A: 2007. The temperature program ramped to 160 ^{o}C in 20 minutes, held for 20 minutes, ramped to 180 ^{o}C in 20 minutes, and held for a final

20 minutes before cooling to ambient for an hour. After cooling, samples were diluted to 50 mL (Kitwe tailings & soil, Akatiti soil) or 100 mL (Akatiti tailings, Uchi tailings & soil) for analysis. Element concentrations were determined by Inductively Coupled Plasma-Optical Emission Spectrometer (iCAP 6200, Thermo Scientific) with settings of 50 RPM analysis pump rate, power: 1150 W, and 5s pump relaxation time.

4.2.5 LEAF pH Dependent Availability

pH dependent availability was determined at target pHs of 2, 4, 5.5, 7, 8, 9, 10.5, 12 and 13 ± 0.5 with a Liquid/Solid (L/S) ratio of 10:1 following US EPA Method 1313 (2017). Briefly, a sample mass of 10 g solid was mixed with 100 mL of leaching solution prepared with ultra-pure water and aliquots of 2M nitric acid or 1M potassium hydroxide for each target pH; shaken end-over-end for 24 hours at 120 RPM; and allowed to settle for 10 minutes. Eluate was centrifuged for 10 minutes at 4000 rpm and measured for pH and electrical conductivity (EC) (Mettler Toledo, MPC 227). If the target pH was not achieved, the process was repeated adjusting the amount of nitric acid or potassium hydroxide. If the target pH was achieved, the sample was passed through 0.45 µm pore size microporous filter, preserved with concentrated nitric acid, and stored at 4 °C. Element concentrations in the aqueous phase were measured by ICP-OES. Chloride (Cl^-) and sulphate (SO_4^{2-}) concentrations were measured by ion chromatography (IC Metrohm, 850 Professional).

4.2.6 LEAF Column Leaching

Dynamic leaching was measured by column leaching tests according to US EPA Method 1314 (US EPA, 2012b). A glass column (50 mm OD, 330 mm H) was packed with sand of average grain size of 2 mm at the bottom to a height of 10 cm followed by 300 g of sample in 5 layers, and finally, another layer of sand at the top covering the same length of 10 cm. The leaching solution was 0.11 mM calcium chloride ($CaCl_2$) prepared in ultra-pure water. Leaching solution was delivered via the bottom of the column using a 2.79 mm ID peristaltic pump (REGLO ICC ISMATEC, Cole-Parmer, UK). After filling the column with leaching solution, it was left for 24 hours to achieve material equilibrium before the actual collection of eluates was initiated.

Eluate samples were collected at L/S ratios (mg/L-dry) of 0.2, 0.5, 1.0, 1.5, 2.0, 4.5, 5.0, 9.5 and 10 at a constant flow rate of 0.208 mL min^{-1}. A sample of 5 mL was taken from each eluate and centrifuged to measure pH and Ec. Remaining eluate was passed through 0.45 µm microporous filter and stored at 4 °C until ICP-OES and IC analysis. Element concentrations were measured by ICP-OES. Bromide (Br^-), chloride (Cl^-), fluoride (F^-), nitrite (NO_2^-), nitrate (NO_3^-), phosphate (PO_4^{3-}) and sulphate (SO_4^{2-}) concentrations were measured by ion chromatography (IC Metrohm, 850 Professional) operating at 1.2 mL min^{-1} with 38 mM KOH in ultra-pure water as eluent.

4.2.7 XRD Analysis

Mineralogical analysis was performed by X-ray diffractometer (Bruker D8 Advance with DaVinci). Samples were air dried and ground to 5 µm particle size in a ball mill. The samples were analysed at 40 V and 40 mA with scan length (2ϕ) of 5 -120 º and step size of 0.5 s. Quantification of the mineral phases was done using Rietveld Refinement method in Total Pattern Analysis Solutions (TOPAS) software.

4.3 RESULTS AND DISCUSSION

4.3.1 Material Characteristics, Copper Content, and Presence of Other PTEs

All tailings and underlying soil material were classified as coarse-grained sands with some gravel and silt present at times (Table 4.1). Tailings all have low organic contents (≤0.8%), which may cause them to have a low buffering capacity (Carvalho, Neiva, Silva and Antunes, 2013; Wang and Mulligan, 2009; Heikkinen and Räisänen, 2009). Underlying soils were similar except for Akatiti soil, which had 5.1%, which may reflect the high kaolinite content identified by XRD rather than soil organic matter. All were neutral to mildly alkaline (7.2≤pH ≤8.5). Akatiti underlying soil was less alkaline than its adjacent tailings, which may indicate mineral weathering (USDA, 2013).

Table 4.1 Physical characteristics of tailings and underlying soils collected from Akatiti, Uchi and Kitwe tailings dams.

Sample location	pH	Moisture content (%)	LOI (%)	Soil classification	Grains distribution
Akatiti tailings	8.47	0.5	0.63	Gravelly sand	Poorly graded
Akatiti soil	7.26	2.14	5.1	Sand soil	Well graded
Kitwe tailings	7.69	0.45	0.6	Silty sand	Well graded
Kitwe soil	8.00	0.23	0.7	Silty sand	Well graded
Uchi tailings	8.06	0.46	0.55	Gravelly sand	Poorly graded
Uchi soil	8.03	0.56	0.8	Silty sand	Poorly graded

Akatiti tailings contain the highest levels of copper (8500 mg/kg), but significant amounts are also found in Kitwe tailings (4480 mg/kg) and Uchi tailings (6200 mg/kg) (Table 4.2). While these concentrations are lower than what would be found in parent rock, all are at levels that would be considered mineral resource elsewhere, which is consistent with previous observations of Copperbelt tailings (Limpitlaw, 1998; Seecharran, 2013). Inefficient extraction from parent rock is a well-documented problem (Dold and Weibel, 2013; Edraki et al., 2014, Falagán et al., 2017 and Muir et al., 2005). Based on these findings, significant copper likely remains in waste tailings with an estimated 380,000 tonnes of copper in Akatiti tailings, 120,000 tonnes at Kitwe, 52,000 tonnes at Uchi Lower, and 3.5 – 6.8 M tonnes of copper from tailings countrywide if other tailings are similar. Extraction of copper from Akatiti tailings has been projected to yield $150 - $180 M in profits (Seecharran, 2013). Kitwe and Uchi tailings seem to offer similar opportunities (Armstrong, 2021). Countrywide, there is approximately 3.5 – 6.8 M tonnes of copper in the tailings if the other tailings sites are similar.

Copper content in underlying soils is also elevated, although more varied. Akatiti soil (680 mg/kg) contains significantly less copper than the tailings, but this concentration is still above the Dutch screening value for soil (Esdat, 2009). Elevated copper likely reflects leaching from the parent tailings. Kitwe and Uchi soils (7600 and 3600 mg/kg, respectively) have elevated copper concentrations similar to their respective tailings (4480 and 6200 mg/kg, respectively), which may indicate mobilisation or based on their similar classifications and compositions (Tables 4.1 and 4.2), these materials may be older tailings. Elevated sulfur in all soils, particularly Kitwe soil (1440 mg/kg) may also indicate weathering and mobilisation, particularly as sulfur in tailings exceeds sulfur in parent materials. Typically, weathering begins with the dissolution of pyrite to release sulphates (Nordstrom and Alpers, 1997). Long exposure to water and air oxidises sulfide minerals, releasing copper and other elements (Sullivan et al., 2005). Lack of vegetative cover may also contribute to weathering.

Some of the other key elements of concern (heavy metals) commonly found in other copper tailings waste had low concentrations in these materials (Table 4.2). Arsenic (8.0-10.0 mg/kg), cadmium (1.0 – 1.3 mg/kg), lead (9 – 11 mg/kg) and zinc (6.3 – 46 mg/kg) in all tailings and soils were below the Dutch Screening Values for soils (Esdat.net. 2009). Apart from Akatiti soil (280 mg/kg), chromium followed this pattern as well (26 – 49 mg/kg). Only copper (550 –

8300 mg/kg) in Akatiti and, in Kitwe and Uchi, copper (3600 – 7200 mg/kg) and cobalt (340–517 mg/kg) were present at levels above the screening values, but they are also opportunities for recovery. In addition to a projected 3.5 – 6.8 M tonnes of copper, tailings may contain 60,800 – 416,000 tonnes of cobalt (76 – 520 mg/kg) for potential recovery. Tailings and soil also contain elevated aluminium, calcium, iron, potassium, magnesium, and sulfur that may require further separation during copper and cobalt recovery and may be valuable to recover as well (Table 4.2).

Table 4.*2* Pseudo-total concentrations of PTEs for Akatiti, Kitwe and Uchi tailings and underlying soils reported as $mgkg^{-1}$ ± sd -dry. Shading indicates exceedances of Dutch Screening Values (Esdat, 2009).

Element	Akatiti tailings	Akatiti soil	Kitwe tailings	Kitwe soil	Uchi tailings	Uchi soil	Dutch Screening Values (Esdat, 2009)
Al	19975.00 ± 593.26	39808.33 ± 2723.09	13639.35 ± 225.28	14460.68 ± 1061.16	13391.87 ± 658.02	14154.00 ± 390.70	76
As	100.50 ± 0.00	1.00 ± 0.00	8.05 ± 0.00	10.02 ± 0.00	5.77645 ± 0.00	8.00 ± 0.00	
Ca	15365.82 ± 777.71	1330.58 ± 64.42	61023.96 ± 930.10	80142.24 ± 4858.20	54526.06 ± 2847.75	52966.67 ± 1686.22	13
Cd	12.56 ± 0.00	0.13 ± 0.00	1.01 ± 0.00	1.25 ± 0.00	0.75345 ± 0.00	1.00 ± 0.00	190
Co	76.00 ± 2.41	29.00 ± 6.5	517.69 ± 10.66	514.35 ± 24.67	343.59 ± 17.55	373.60 ± 15.32	180
Cr	49.62 ± 2.41	279.42 ± 121.28	30.18 ± 0.53	31.99 ± 1.67	25.52 ± 1.48	27.87 ± 1.36	190
Cu	8500.15 ± 456.24	675.00 ± 56.23	4508.89 ± 50.78	7645.04 ± 373.36	2634.28 ± 164.36	3582.00 ± 244.10	
Fe	25212.30 ± 887.82	47791.67 ± 10042.17	15569.53 ± 227.01	19564.90 ± 1012.33	13736.51 ± 689.08	14996.00 ± 549.72	
K	14612.07 ± 577.99	1484.58 ± 42.71	11518.70 ± 164.31	11964.96 ± 695.66	9123.02 ± 613.64	12435.33 ± 416.99	
Mg	26896.31 ± 844.46	2248.42 ± 59.20	39737.00 ± 575.80	46815.76 ± 2687.86	39249.16 ± 1985.51	37420.00 ± 1092.34	
Na	678.38 ± 0.00	67.50 ± 0.00	54.32 ± 0.00	67.66 ± 0.00	80.368 ± 0.00	54.00 ± 0.00	100
Ni	48.37 ± 3.77	40.83 ± 2.50	18.31 ± 0.40	20.38 ± 0.81	14.33 ± 3.55	17.47 ± 0.64	
P	1169.57 ± 39.49	287.50 ± 34.98	705.27 ± 34.47	1064.02 ± 71.76	563.15 ± 26.09	600.47 ± 29.95	530
Pb	108.04 ± 0.00	10.75 ± 0.00	8.65 ± 0.00	10.77 ± 0.00	7.09 ± 0.83	8.60 ± 0.00	
S	532.02 ± 69.85	198.50 ± 12.31	2375.50 ± 295.32	1441.31 ± 115.18	1065.22 ± 328.72	492.00 ± 65.21	
Zn	6.28 ± 2.51	45.58 ± 1.88	19.92 ± 0.20	22.30 ± 1.56	20.52 ± 1.18	23.07 0.95	

NB: Results are reported as mean ± 1 SD dry weight (n=3)

Interestingly, XRD analysis did not identify any copper or cobalt minerals in tailings or bottom soils (Table 4.3) despite elevated total copper and cobalt levels (Table 4.2). This may be because individual copper and cobalt minerals fall below detection limits; these elements are present in sorbed rather than mineral forms; or a combination of these things. Further mineralogical analysis would be beneficial.

Table 4.3 Mineral phase identification for Akatiti, Kitwe and Uchi Tailings.

Soil type	Mineral phase present	Percentage Composition (%)
Akatiti tailings	Mica (biotite and muscovite)	37.71
	K-Feldspar	43.86
	Quartz	18.42
Akatiti bottom soil	Mica (biotite and muscovite)	10.80
	K-Feldspar	1.43
	Kaolinite	43.20
	Quartz	44.57
Kitwe tailings	Mica (biotite and muscovite)	22.77
	K-Feldspar	4.95
	Calcite	2.54
	Dolomite	18.67
	Quartz	17.90
	Gypsum	0.69
	Chlorite	4.4
Kitwe bottom soil	Mica (biotite and muscovite)	7.51
	K-Feldspar	41.71
	Feldspar	5.17
	Calcite	3.77

	Dolomite	14.86
	Quartz	19.35
	Kaolinite	3.18
	Chlorite	4.45
Uchi tailings	Mica (biotite and muscovite)	16.13
	K-Feldspar	31.38
	Feldspar	8.47
	Calcite	5.74
	Ankerite	17.27
	Dolomite	2.47
	Quartz	14.62
	Clinochlore	3.81
Uchi bottom soil	Mica (biotite and muscovite)	17.34
	K-Feldspar	27.21
	Feldspar	6.02
	Calcite	3.73
	Ankerite	2.82
	Dolomite	25.68
	Quartz	15.49
	Vermiculite	1.71

4.3.2 pH dependent availability of copper and other PTEs

pH-dependent availability profiles of copper and cobalt in tailings and underlying bottom soils are shown in Figure 4.1. Copper exhibited amphoteric leaching profiles in tailings and soils with elevated concentrations at lower acidic conditions ($2 \leq pH \leq 4$) and higher alkaline conditions ($12 \leq pH \leq 13$) in all materials. Copper is most easily removed in highly acidic and highly alkaline conditions, which is consistent with acid mine drainage conditions that have been documented in the Copperbelt (SGAB et al., 2005). Cobalt exhibited cationic leaching behaviour in all tailings and bottom soils, which means elevated concentrations of cobalt were released in acidic conditions ($pH \leq 4$) and significantly less in mildly acidic to neutral and alkaline conditions ($5.5 \leq pH \leq 13$). Sulfur availability seemed independent of pH in Akatiti and Uchi tailings and soils, suggesting highly soluble leaching behaviour independent of pH. Sulfur availability exhibited step change decreases at $7 \leq pH \leq 8$ in Kitwe tailings and $8 \leq pH \leq 10$ in Kitwe soil. Sulfur availability relatively independent of pH may also indicate potential for acid mine drainage conditions to develop at these sites.

Aluminium and zinc exhibited amphoteric leaching in all materials except for Kitwe tailings, which exhibited more cationic leaching. More zinc was released at $pH \leq 4$ in all the tailings sites indicating that zinc is easily removed in the acid conditions than in the neutral or alkaline conditions.. None of these elements are present above concentrations of concern in tailings or soils (Table 4.2).

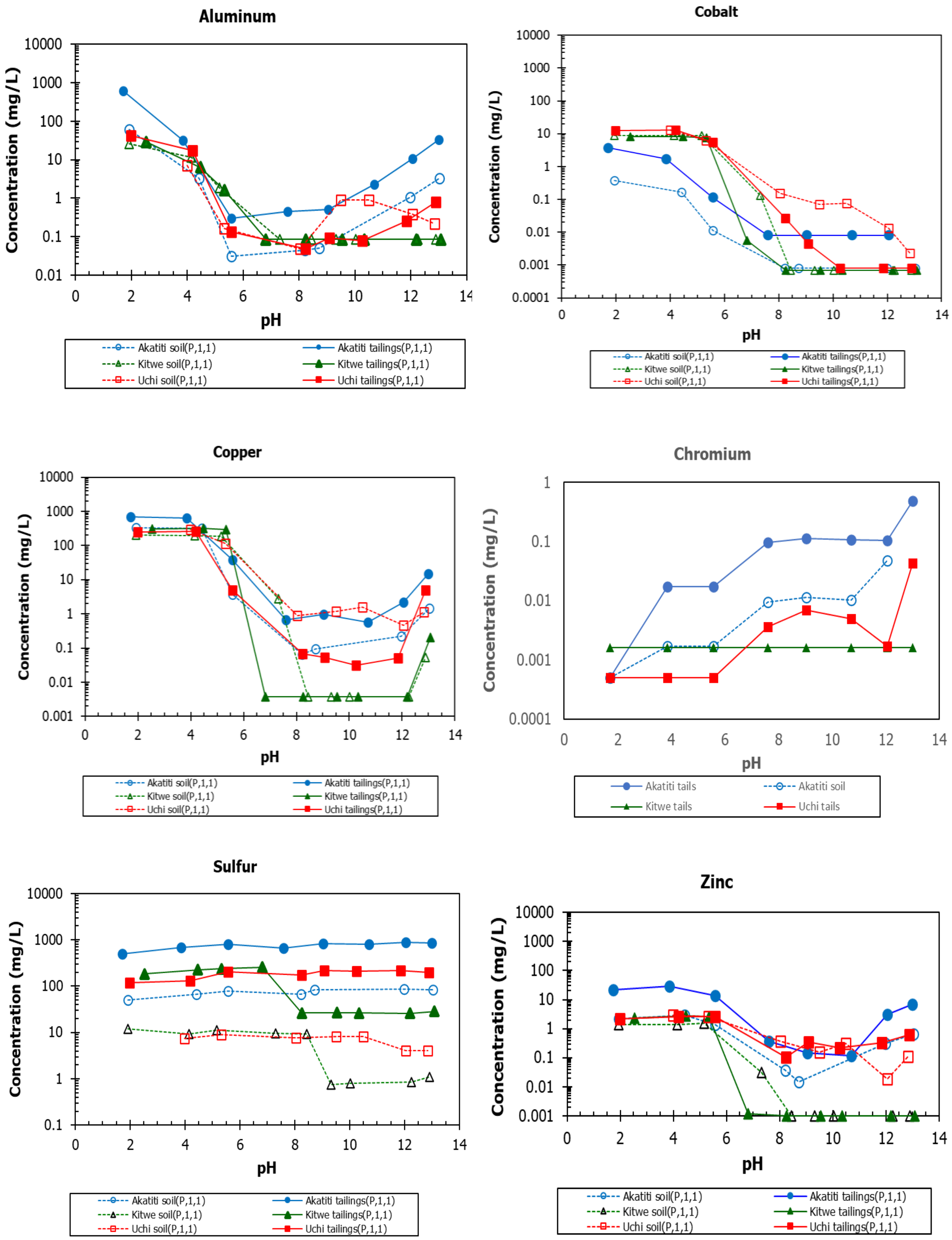

Figure 4.1 pH dependence leaching profiles of Al, Co, Cu, Cr, S and Zn for Akatiti, Kitwe, and Uchi tailings and their bottom soils at 2 ≤ pH ≤ 13 plotted using Leach XS software.

The higher availabilities observed for some elements such as copper may be caused by the formation of oxyanions or cations which can make them more susceptible to leaching (Chen et al., 2012 and Cornelis et al., 2008 cited by Cui et al., 2019) or by oxidation reactions of mineral bounds attached to these PTEs which are dissolving to a more water-soluble metallic hydroxide compounds via adsorption processes (Al-Abed, 2006). Examples of these highly soluble hydroxide complexes include $Cu(OH)_2$ and $Co(OH)_2$) (US EPA, 2017). The hydroxide complexes may be acting as catalysts to dissolve metals in the aqueous solutions. Further mineralogical analysis would be beneficial to explore this hypothesis.

While concerning from an environmental point of view, this leaching behaviour is promising from a resource recovery point of view. If it is available, copper can be recovered and put to beneficial use. At 10:1 L/S ratio, recoveries of 83% for Akatiti tailings at pH 2, 73% for Kitwe tailings at pH 4 and 43% for Uchi tailings at pH 4 were observed. These recoveries are not high enough to bring residual copper concentrations in extracted tailings below the Dutch screening value for soil (190 mg/kg); however, higher recoveries may be possible at higher L/S ratios and may achieve this objective.

Copper leaching potential, especially for Akatiti and Kitwe tailings, likely reflects weathering and oxidation of copper sulfide compounds into more acid-soluble oxide compounds. The molar mass ratio of copper and sulfur was calculated as 8.09 for Akatiti tailings, representing 8x more copper than sulfur, which indicates either more weathering or less copper sulfides in the parent material. Mining in Luanshya started in the early 20th Century after the discovery of copper deposits along the banks of the Luanshya River (Harrop, 2022) and early mining activities targeted surface deposits with copper oxide ores. Akatiti tailings may be from mining these surface deposits, which may be why leachability of copper is higher compared to Kitwe and Uchi tailings. In comparison, the copper to sulfur ratios of Kitwe and Uchi tailings was 0.94

and 0.95, respectively. These characteristic differences may reflect different mineral profiles at Akatiti (Luanshya) than Kitwe and Uchi (Kitwe), or more weathering at Akatiti compared to the others. Akatiti tailings dam may also be older than the other two. Differences between Kitwe and Uchi tailings were also apparent. At pH 2, significantly more copper is available from Kitwe tailings (73%) compared to Uchi tailings (43%). This difference is important for both remediation and recovery.

In contrast to copper, cobalt recovery at pH 2 is limited (49%, 16%, and 36% from Akatiti, Kitwe, and Uchi tailings, respectively) and residual cobalt concentrations still exceed the Dutch Screening Value for soil (190 mg/kg). While more cobalt may be recovered at higher L/S ratio, it may not reach the high copper recoveries achieved, particularly from Akatiti and Kitwe tailings. Apart from Akatiti cobalt concentrations, which are already below 190 mg/kg, mild acid extraction seems unlikely to achieve this threshold on its own. Other strategies for recovering or remediating cobalt are necessary.

At pH 2-4, elevated concentrations of calcium and magnesium are also observed in extracts and would require separation from the copper solution to facilitate its beneficial use. Additional information on the recovery potential of mineral elements at pH 4 is shown in Table 6 under Appendix F for Akatiti, Kitwe and Uchi tailings.

4.3.3 Column leaching of copper, cobalt and other PTEs

Most PTEs in the column leaching experiment exhibited low available content in the eluates, which reflects the relatively neutral pH during the test (Figure 3-G in Supplementary Materials, Appendix G) and low availabilities in this pH range (Figure 4.1). At neutral pH, copper and other PTEs may be present as insoluble hydroxide complexes and thereby inhibiting oxidation processes (Malviya and Chaudhary, 2006; Eighmy et al., 1995). Copper and cobalt releases provide illustrative examples (Figure 4.2).

The amount of copper available in the leachates ranged from below detection limits to 0.018 mg/L and total copper collected in the eluates was <<0.01% pseudo total content in all materials (0.044 mg/kg-dry, 0.078 mg/kg-dry and 0.145 mg/kg-dry from Akatiti, Kitwe and Uchi tailings, respectively) (Figure 4.2). Uchi tailings exhibited the most copper release followed by Kitwe and then Akatiti. All three tailings exhibited early washout of copper followed by slower continued release. Copper release increased again in Akatiti and Uchi tailings, although all three release profiles seemed to exhibit availability-limited behaviour by the end of the experiment. Leachate pH ranged from 6.0 to 8.0 (Table 5, Appendix E), which is consistent with the low availability range in the pH-dependent tests (Figure 4.1). Based on the availability profiles, more copper would likely be released if the experiment continued longer or pH was lower, likely reflecting prolonged slow release which may cause acid mine drainage from the tailings into the surrounding environment. Local factors such as acid rain may increase copper release (Mwaanga et al., 2019).

Sulfur releases from Kitwe and Uchi tailings were greater than release from Akatiti tailings (Appendix H, Figure 4-H). Early washout of sulfur from Kitwe and Uchi tailings suggest weathering processes that may take longer to develop as compared with Akatiti tailings. Kitwe tailings had 90 mg/kg-dry tailings of sulfur available in the leachate at 0.2 L/S ratio (i.e., the initial stages of the experiment, at test position one) and the concentration decreased as the experiment progressed with time until at a cumulative L/S ratio of 9.5 (i.e., at test position eight) where a concentration of 18.19 mg/kg-dry tailings was leached. Uchi tailings had the highest concentration of sulfur released in the leachate with a concentration of 145.09 mg/kg-dry tailings at 0.2 L/S ratio and its concentration decreased as the experiment progressed but far from depletion with a mass release of 86.27 mg/kg-dry tailings in the last fraction of the eluate collection at (cumulative Liquid-to-Solid ratio of 10. The leaching profile of sulfur for Akatiti tailings depicted a solubility controlled leaching whose release was dependent on the increase of the liquid/solid ratio. The total amount of sulfur collected in the eluate for Akatiti tailings at 9.5 cumulative L/S ratio shows that prolonged weathering is possible.

The high availability of sulfur in the leachates from all tailings indicates possible acid mine drainage conditions are developing, which may lead to further dissolution of copper and cobalt over time.

Cumulative releases of sulphate ions discharged in the eluates for Akatiti, Kitwe and Uchi tailings were 630 mg/kg- dry tailings (1.44 mmol), 12240 mg/kg- dry tailings (19.04 mmol) and 42650 mg/kg- dry tailings (66.30 mmol), respectively (Appendix H, Figure 4-H). Higher amounts of sulphate (SO_4^{2-}) ions available, especially in Uchi tailings, is an indication of high oxidative dissolution. Ore release of more sulphate ions ($SO_4{}^{2-}$) is often accompanied by more release of metals (Fe^{2+} and others) and possibly protons (H^+) to solution (Nordstrom and Alpers, 1997) as acid mine drainage, potentially affecting groundwater and surrounding surface waters (Bashir, 2012; Hageman, 2005; He et al., 2015; Patricio et al., 2009; Servida, 2009).

Cobalt release in all tailings was very low with cumulative totals of 0.0087 mg/kg-dry for Akatiti (0.011%), 0.022 mg/kg-dry for Kitwe (0.004%), and 0.020 mg/kg-dry for Uchi tailings (0.005%). Early washout of cobalt was observed for Kitwe and Uchi tailings while prolonged release was observed for Akatiti tailings; however, all release profiles became availability limited. Small releases were also observed for aluminium and chromium. Total releases of aluminium were 0.039 mg/kg (0.0002%), 0.089 mg/kg (0.0007%), and 0.095 mg/kg (0.0009%) for Akatiti, Kitwe, and Uchi tailings, respectively. Early washout of aluminium was observed for Kitwe and Uchi tailings whereas Akatiti tailings showed a prolonged release behaviour. Availability limited release of aluminium was observed in all tailings.

Accumulation of PTEs in the eluates is an indication that PTEs are being washed from the tailings into the surrounding soils and water bodies. The tailings material may also be undergoing weathering of pyrite or other sulfide minerals leading to the formation of hydrous iron sulphate such as melanterite ($FeSO_4 \cdot 7H_2O$) and zinc sulphate salts e.g., goslarite ($ZnSO_4 \cdot 7H_2O$) (Blowes et al., 1991; Hammarstrom et al., 2005), which, in turn, can lead to significant dissolution of copper, cobalt, and other PTEs as well as hydrogen atoms (H^+) into receiving waters (Jambor et al., 2000). Evidence of formation of acid mine drainage conditions may explain the presence of copper, cobalt and other elements that have been found in rivers and streams around Kitwe (Sracek et al., 2012) and elsewhere in the Copperbelt.

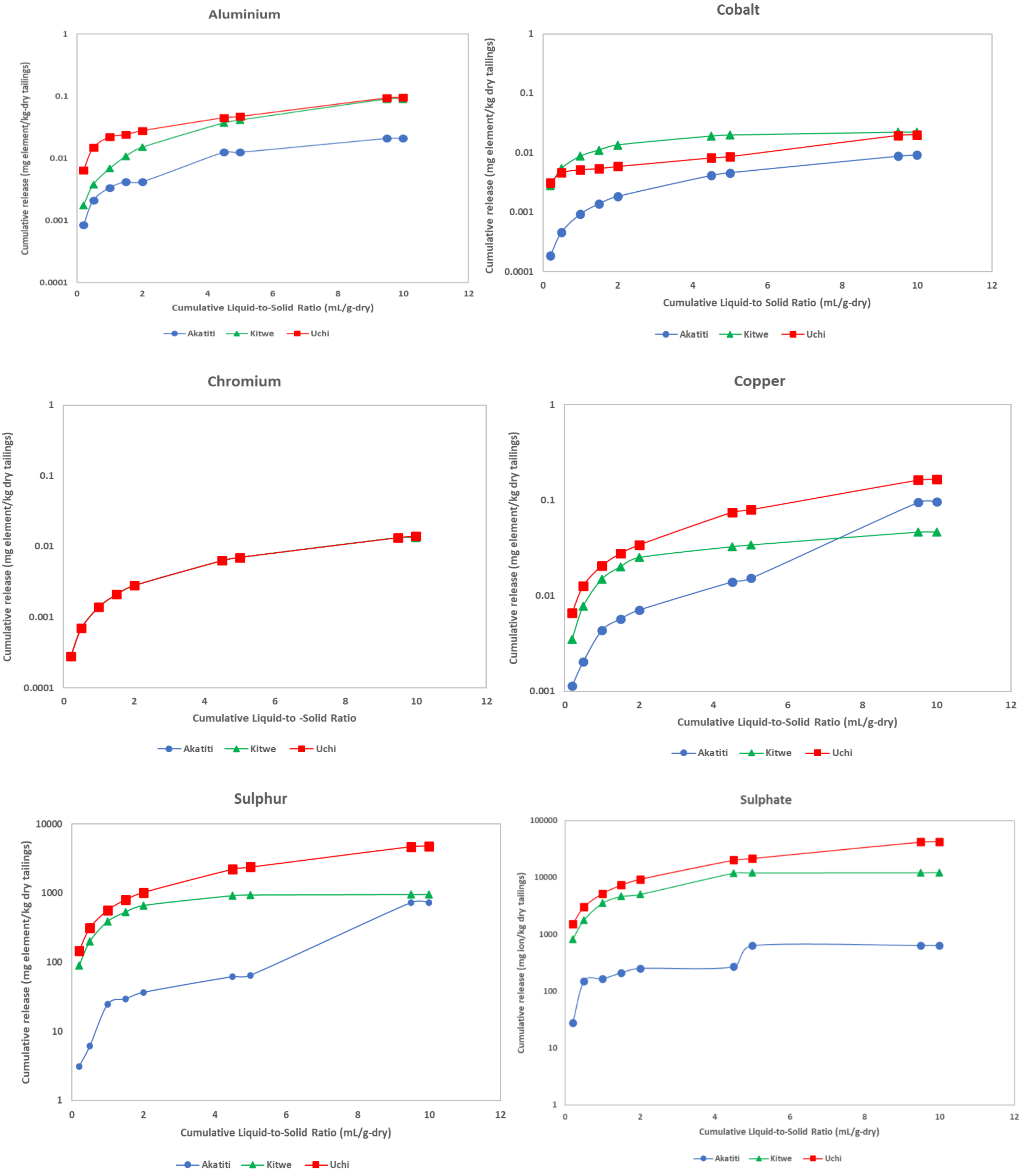

Figure 4.2 Cumulative release of aluminium, cobalt, chromium, copper, sulfur and sulfate as a function of liquid to solid ratio via column leaching for Akatiti, Kitwe and Uchi tailings.

4.3.4. Recovery Potentials of Copper and Cobalt

Copper and cobalt are key mineral resources of value driving past and current mining in the Copperbelt. Their recovery as part of remediation may be beneficial as a key driver in managing PTEs in the tailings of the Copperbelt, providing economic incentive in addition to potential regulatory obligation. Significant copper (2700 – 7050 mg/kg-dry tailings) and some cobalt (37 – 82 mg/kg-dry tailings) can be extracted at lower pH levels (pH ≤ 4) from some tailings. Extraction of copper from the tailings is advantageous because of its high concentrations and presence in crushed form which can save on comminution processes (i.e., crushing and grinding) than mining from intact rock. Extractions of cobalt are relatively inefficient and further recovery processes may be necessary to recover more from the tailings. Further characterisation of the tailings needs to be conducted to identify the copper forms (mineral or sorbed) so that these findings can be applied to other tailings on the Copperbelt and elsewhere.

4.4 CONCLUSIONS

Elevated levels of copper are present in Akatiti, Kitwe, and Uchi tailings and Kitwe and Uchi bottom soil comparable to what is considered ore in other places. Elevated cobalt is also present in Kitwe and Uchi tailings, likely reflecting differences in the parent ore bodies in comparison to Akatiti, which is low in cobalt. Elevated copper and cobalt concentrations are high enough to be considered environmental contaminants and some evidence of their mobility in the aquatic environment has been noted by others. Low levels of other PTEs (Cd, Cr, Pb, and Zn) are present in the tailings, which makes the recovery of copper and cobalt appealing as part of or in addition to remediation. pH dependent availability tests showed elevated levels of copper at pH ≤ 4 and pH ≥12, indicating a strong dependence on the acidity or alkalinity of the leaching solution. These availabilities in the pH extremes likely reflect the ability of all tailings to form acid mine drainage conditions but also may provide means for copper recovery. Extraction efficiencies for copper were 83%, 73% and 43% from Akatiti, Kitwe and Uchi tailings. Based on these findings, significant copper likely remains in waste tailings with an estimated 380,000 tonnes of copper in Akatiti tailings, 120,000 tonnes at Kitwe, 52,000 tonnes at Uchi Lower, and 3.5 – 6.8 M tonnes of copper from tailings countrywide if other tailings are similar. Cobalt recovery was limited, with 49%, 16% and 36% recoveries for Akatiti, Kitwe and Uchi tailings. However, these extraction values of copper and cobalt leaves significant levels in the parent tailings, still above the safe limits, so additional work is necessary to improve these recoveries. The column dynamic leaching tests show relatively low levels of copper, cobalt and other PTEs released in the eluates at native conditions; however, relatively high levels of sulfur show that acid mine drainage conditions are likely forming and further releases of copper and cobalt into the environment may follow. The presence of elevated copper and cobalt in the underlying soils shows that some releases through acid mine drainage may have occurred already in the field. Remediation of these tailings dams is critically necessary, and this work shows that recovery of copper and cobalt may be possible as part of this remediation.

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5.0 CHAPTER 5 ENERGY EFFICIENT ROASTING AND REMEDIATION OF COPPER MINE TAILINGS VIA SMOULDERING

ABSTRACT

Smouldering and roasting were evaluated for the recovery and treatment potential of copper and cobalt as well as understanding their influences on the fate of other potentially toxic elements (PTEs) such as calcium, magnesium, potassium, phosphorous and sulfur from copper sulfide tailings from Akatiti and Uchi tailings dams from Copperbelt Province, Zambia. Roasting is sometimes used to enhance copper extraction via hydrometallurgical processes. Smouldered tailings were prepared by mixing tailings with sand, 10% water, and 5% vegetable oil and smouldering in a column, yielding peak temperatures of 390 - 770°C and 450-600 °C for Akatiti and Uchi tailings, respectively. Roasted tailings were produced by exposure to 600 °C or 1000 °C in a muffle furnace for 4 hours. Leaching Environmental Assessment Framework (LEAF) Methods 1313 and Method 1314 were used to assess the leaching potential of PTEs before and after treatment; for the roasted tailings, a subset of Method 1313 test positions was used. After smouldering, PTEs including copper and cobalt became less available across the pH domain 2 ≤ pH ≤ 13, which may aid in the environmental remediation goal of preventing mobilisation. Roasting at 600 and 1000 °C had similar effects on Akatiti tailings, which is useful for remediation but less so for copper recovery; however, these tailings are readily extractable at pH ≤ 4, so enhancement was not necessary. After roasting Uchi tailings at 600 °C, extraction of copper improved from 43% to 63% at pH = 4, which suggests further exploration of low temperature treatment may be beneficial for enhancing acid leaching recovery of copper from these tailings. Nevertheless, combined remediation and resource recovery using either smouldering or roasting on its own was unmet in this research. Different approaches are likely required for remediation and resource recovery from tailings on the Copperbelt.

Keywords: Smouldering; Roasting; Copper tailings; Remediation; Resource recovery

5.1 INTRODUCTION

The mining industry is regarded as one of the major contributors of pollution to the environment. The sector is responsible for releasing not only potentially toxic species such as nitrogen oxides and sulfur dioxides to the environment but also leaves behind a legacy of solid wastes such as tailings, and slag (Hudson-Edwards et al, 2011). Copper mine tailings are waste solids generated during crushing, milling, and other processes used to recover copper from mined ore (Geng et al., 2017). Extraction of the copper ore is often done by flotation processes which separate the ore from the waste at the concentrator: the ore floats to the top in air bubbles and the waste materials sinks to the bottom as tailings (Will's, 2016; Dhir et al., 2017).

Zambia's Copperbelt has rich copper reserves up to 3% by mass (Bowen and Gunatilaka, 1933; Kamona and Nyambe, 2002 cited in Africa, 2011). Mining in Zambia started in the early 1920s, but due to inefficient recovery processes, it generated waste tailings that remain embedded with copper at levels that are comparable to ores in other regions (Seecharran, 2013). Reports of 0.24% of copper ore grade have attracted investment in remining Luanshya tailings (Proactive Investors UK, 2021). This research has shown that some tailings dams have higher copper concentrations (Chapter 4). Tailings dams are distributed throughout the Copperbelt with about 791 million tonnes covering 9,125 hectares of land (Environmental Council of Zambia, 2008 cited in Lindah, 2014). In the neighbouring Democratic Republic of the Congo, where the Central African Copperbelt extends, informal economies have developed around tailings sites to recover copper due to its high concentrations in tailings (Lutandula and Maloba, 2013).

Communities surrounding the tailings dams are often impacted by leaching of copper and other potentially toxic elements into ground and surface waters. In 1981, a spillage of mine tailings into the Mwambashi River led to the water pollution of the Kafue River (Muloiso and Zulu, 1993), one of the main sources of water for the Copperbelt region supplying about 40%

of water resources in the region (Ngulube et al., 2016). Elevated levels of potentially toxic elements have been reported in the Nchanga and Mushishima Rivers of Chingola and the Uchi and Wanshimba Rivers of Kitwe town (Kosgei et al., 2020).

In Zambia, copper mining is carried out by open pit mining mostly for copper oxides and by underground mining for copper sulfides. Copper is most commonly present in the earth crust as copper-iron-sulfides and copper sulfides, including chalcopyrite ($CuFeS_2$) and bornite (Cu_5FeS_4) and chalcocite (Cu_2S) respectively (Davenport et al., 2002). Generally, copper is extracted by hydrometallurgy for oxides and pyrometallurgy for copper sulfides. Pyrometallurgical processes are used for copper sulfide extraction because hydrometallurgy tends to have slow dissolution kinetics of chalcopyrite and other sulfide minerals (Panda et al., 2013; Wan et al., 2020). Extraction of copper using hydrometallurgical processes involves the use of aqueous solution such as dilute sulfuric acid (Hocking, 2006) while pyrometallurgical processes consist of smelting and other thermal processes (Mishra, 2001). Roasting is a thermal enhancement process that is sometimes used to enhance the recovery process of copper sulfides for subsequent hydrometallurgical processing. Smelting involves the application of heat to ore to extract the desired base metal at a higher temperature above its melting point by concentrating the metal and removing impurities in each processing step (Ramanayaka, et al., 2020).

Roasting is an oxidation process applied before leaching to decompose sulfide minerals at elevated temperatures leading to a higher extraction of metals in dilute acidic solvents (Prasad and Pandey, 1998). Most copper and cobalt ores on the Zambian Copperbelt contain sulfide compounds which cannot be easily extracted with dilute sulfuric acid. Copper sulfides are roasted so that they can be oxidised to form copper oxides that can be leached by acids and extracted by electrolytic deposition (Green and Ariz, 1971; Güntner and Hammerschmidt, 2012). During roasting, ores or concentrates are heated which causes a reaction leading to the formation of a volatile matter such as sulfur dioxide which can be captured and used in sulfuric acid production (Thomas and Cole, 2016). During roasting, copper concentrates may undergo transformations to minerals such as copper sulphates that are acid soluble (Cocić et al., 2011) and iron from the sulfide ore is converted to an oxide form (Fe_2O_2 or Fe_2O_3) that is partially insoluble in acid and is discarded as waste in the tailings (Güntner and Hammerschmidt, 2012).

Mine reclamation is considered as one of the final stages in the life of a mine to remediate contaminated soils and restore the mine and its surroundings after all the mining activities have been completed. Existing methods for mine tailings remediation include backfilling in open excavations (Wills, 2016) and phytoremediation to extract or stabilise PTEs (Moskvitch, 2014; Karaca et al., 2017). However, these remediation approaches have limitations (Chapter 2, Section 2.4). None wholly solves the complex requirements of mine tailings management or harnesses the benefits of recovery of copper and other elements. Therefore, further work is necessary to ensure safe management and remediation of mine tailings in the Zambian Copperbelt and elsewhere is achieved and opportunities for copper recovery from waste materials are not overlooked. Smouldering may provide an energy-efficient alternative to roasting to enhance recovery and/or used as remediation technique. To the knowledge of the authors, application of smouldering as a remediation or extraction technique to treat PTEs contained in copper mine tailings has not been explored.

Smouldering is a flameless form of combustion that occurs at the surface of a solid or liquid fuel (Ohlemiller, 1995; Rein, 2016). Remediation of soils contaminated with hazardous organic liquids using smouldering is an emerging technology that is patented (Pironi et al., 2009; Switzer et al., 2009; Switzer et al., 2014). The majority of smouldering research focuses on solid fuels such as coal, charcoal, and peat (Busmaster, 1996; Ohlemiller, 1995; Rein et al., 2005). In more recent studies, smouldering has been applied to treat high moisture content biosolids such as sewage sludge (Rashwan et al., 2016; Ronda et al., 2019) and recover valuable phosphorus and other elements (Fournie et al, 2021).

Smouldering is an energy efficient and self-sustaining method for soil treatment and waste management because of the following main features. Firstly, it usually does not require supplementary energy after ignition. Secondly, the high energy-efficiency of the process allows for a self-sustaining process even with a material that has low calorific contents (Wyn et al., 2020). Examples of feedstocks that have achieved self-sustaining smouldering with low calorific fuels include biosolids mixed with sand at 1.6 MJ/kg (Rashwan et al., 2016), crude oil mixed with sand at ~1.4 MJ/kg and coal tar mixed with sand at ~1 MJ/kg (Wyn et al., 2020). Smouldering can remove 99.9+% of hydrocarbons or other contaminants in a contaminated soil or other porous media (Pironi et al., 2011 and Switzer et al., 2009, Scholes, 2013, Yerman et al., 2015 and Rashwan et al, 2016). This combination of features may make it more energy efficient than roasting. Tailings do not contain sufficient carbon to smoulder on their own, but supplemental fuel can be mixed with tailings to support smouldering.

The aim of this research was to evaluate the recovery and remediation potential of PTEs such as copper, cobalt, sulfur and phosphorous using thermal treatments. Smouldering and roasting effects were evaluated for changes to total composition and availability of copper, cobalt, and other PTES. The LEAF leaching protocols (Method 1313, pH dependence leaching and Method 1314, column dynamic leaching) were used to evaluate these effects.

5.2 METHODOLOGY

5.2.1 Materials and sample preparation methods

Copper tailings were obtained from Akatiti and Uchi tailings dams (-13.138S, 28.399E and -12.831S, 28.224E, respectively) from the Copperbelt Province of Zambia. The tailings from the two sites were classified as coarse-grained sands with some gravel and silt, low organic content (≤0.8%), and, therefore, likely low buffering capacities for the PTEs they contain (Chapter 4).

5.2.1.1 Smouldering treatment

To prepare for the smouldering tests, tailings were manually mixed at a ratio of 1:1 with sand with 1.34 mm mean grain size, 1700 kg m^{-3} bulk density, 40% porosity and a coefficient of uniformity 1.35 (Leighton Buzzard 8/16; Switzer, et al., 2009). The tailings and sand mixture was further mixed with 10% water by mass to help with the heat transfer and 5% sunflower oil by mass to act as fuel.

Smouldering was carried out in a quartz glass column measuring 13.8 cm in diameter and 40 cm height following the established procedures of Switzer et al (2009) and Pironi et., (2011). An Inconel cable heater (75 cm in length) with voltage and energy inputs of 240 V and 450 W from Watlow Ltd, UK was used. Sand was packed to about 5 cm in the quartz column then an air diffuser placed on top of the sand and an extra 2 cm clean sand was added to cover the air diffuser. The Inconel heater was coiled into a flat spiral and placed at the top of the clean sand. The fuel and tailings mixture was then added on top of the heater to about 24 cm. Clean sand was added on top of the fuel mixture to about 5 cm to absorb expanding liquid.

To monitor the self-sustaining ignition of the smouldering front and peak temperatures, thermocouples were inserted along the centre of the column at 4 cm apart with the first thermocouple (TC1) placed at 4 mm away from the heater. To initiate the smouldering process heat energy was applied to the treatment media for 90 minutes. After 90 minutes of heating, compressed air was then introduced at an air flux of 3.79 cm/s via the air diffuser and direct energy to the heater from the power source was ceased by switching off the power source.

5.2.1.2 Roasting using the muffle furnace

Tailings specimens of 200.0 g ± 0.1 g of air-dried tailings were roasted in the muffle furnace at 600 °C and 1000 °C for 4 hours respectively in an evaporation dish. The specimens were placed in the furnace at the start of the temperature programme until the 4 hours of heating had elapsed. Specimens were left in the furnace until they had cooled down to room temperature (20°C) and were removed from the furnace the next day.

5.2.1.3 PTE concentration via aqua-regia

Samples of 0.2 g were used to determine elemental composition of the potentially toxic elements after roasting. Tests were done in duplicate for the 600 °C roasted samples and for the 1000 °C temperature. Samples were digested in 10 mL modified aqua regia (1:4 HCl: HNO_3) in a microwave digestion system (MARS Xpress) following EPA 3052. The temperature program ramped to 160 ºC in 20 minutes, held for 20 minutes, ramped to 180 ºC in 20 minutes, and held for a final 20 minutes before cooling to ambient for an hour. The final volume of the sample after microwave digestion was diluted to 100 mL in a volumetric flask with deionised water. The sample was further diluted by a factor of 10 for ICP-OES analysis.

5.2.1.4 pH Dependent Availability

pH dependent availability was conducted following US EPA Method 1313 (EPA, 2017) on the untreated and smouldered tailings of Akatiti and Uchi tailings. Samples were prepared by sieving with a 2 mm BS sieve. For each test position, a liquid/solid ratio of 10 L/kg was prepared by combining 10 g tailings and 100 mL of extraction solution in 125 mL polyethylene bottles. Each extraction solution was prepared to the specified pH ranging from $2 \leq pH \leq 13$ by varying 2M of HNO_3 for acidity or 1M of KOH for alkalinity. The bottles were tumbled at 120 rpm end-over-end for 24 hours. After shaking, the bottles were removed and settled for 10 minutes before centrifuging.

An aliquot of 10 mL was extracted from each bottle, placed in 50 mL centrifuge tube, and centrifuged at a speed of 4000 rpm for 10 minutes. pH and Electrical conductivity (Ec) were measured using a combined pH/conductivity meter (Mettler Toledo, MPC 227). If the desired pH was achieved, the remaining samples from the 100 mL polyethylene bottles were filtered using a 0.45 µm microporous filter and preserved by adding a drop of highly concentrated nitric acid and stored in the cold room at 4 °C waiting for further analysis. If the target pH was not achieved, the solution was discarded and the process was repeated with fresh sample and adjusted extraction solution. Nine test positions ($2 \leq pH \leq 13$) were prepared for the untreated and smouldered tailings. A subset of the pH targets ($2 \leq pH \leq 5.5$) was prepared for the roasted tailings.

5.2.1.5 Column Leaching

An up-flow column leaching method 1314 (EPA, 2012) was used to evaluate the leaching potential of PTEs before and after smouldering treatment. To prevent clogging in the peristaltic pump tubes, leaching solution was prepared with 0.11 mM of calcium chloride in ultra-pure water. Sand with particle size ≤ 2 mm was packed at the bottom of the borosilicate glass column measuring 50 mm inner diameter and 330 mm height. Then 300 g of sample both for the untreated and treated tailings were packed in 5 layers on top of the sand in separate experiments. After that, the sample material was covered with more sand. A 3-phase channel peristaltic pump with 2.79 mm tubing was used to deliver leaching solution to the column from a 2000 mL borosilicate glass bottle. The leaching solution was passed through the glass column containing the sample and upon reaching the top of the column the pump was stopped and left for 24 hours to achieve equilibrium. Eluates were collected at a flow rate of 0.208 mL/min at specified L/S ratios of 0.2, 0.5, 1.0, 1.5, 2.0, 4.5, 5.0, 9.5, and 10.0 mL/g-dry tailings.

5.2.1.6 Normalisation of results

The reported results on total and available contents in the eluates before and after treatment were normalised considering moisture content for the untreated tailings and mass losses for the treated tailings. Furthermore, after smouldering, the sample specimen was assumed to be completely dry due to the peak temperatures attained during treatment and there was no presence of moisture and oil, which were consistent with visual inspection. There was no smell of oil, fresh or burnt, and no apparent wetness. Mass losses from smouldering were corrected using 600 °C from the roasting process because some mass loss from heating was expected and it was the closest temperature smouldering had reached.

5.3 RESULTS AND DISCUSSION

5.3.1 Effects of roasting and smouldering on mine tailings

Roasting at 600 ºC and 1000 ºC resulted in average mass losses of 1.2 % and 4.0 % in Akatiti tailings and 1.6 % and 11 % in Uchi tailings (Appendix I, Table 5.3). Colour change in the tailings was observed from greyish to brown and golden brown at 600 °C and 1000 °C, respectively, in both tailings. Smouldering achieved peak temperatures of 390 – 770 ºC in the Akatiti tailings mixture and 450 – 600 ºC in the Uchi tailings mixture (Appendix I, supplementary data, Figures 5-I and 6-I). Smouldering was not self-sustaining, which happens sometimes in laboratory tests that would not necessarily happen at larger scale (Switzer et al., 2014). Some heat losses were observed, especially near the top thermocouples, which is expected at laboratory scale of operation (Rein et al., 2009; Switzer et al., 2014; Williams, 1977). This is caused by a larger surface area per unit volume of the smouldering mass in a column than when the operation is scaled-up. In addition, heat losses are caused by non-uniform air fluxes at the top of the column (Rashwan et al., 2020). The inefficiency of achieving a consistent peak temperature could be caused by low organic matter (i.e., insufficient fuel) in the materials or operating conditions (Switzer et al., 2009). Visual inspection showed removal of the oil and colour change of the materials from grey (tailings) and yellow (sand) to reddish brown (tailings) and red (sand) (Figure 5.1).

Figure 5.1 Before (Left) and After (Right) Smouldering of Akatiti tailings.

The average smouldering propagation velocities attained for Akatiti and Uchi tailings were 0.3 cm/min and 0.2 cm/min respectively, which were slower than what has been observed in other analogous smouldering remediation systems at laboratory scale (Pironi et al., (2009), Rein, (2009) and Switzer et al., (2009)) but consistent with systems experiencing inefficiencies (Switzer et al, 2014).

5.3.2 Total PTEs before and after treatment

5.3.2.1 Smouldered tailings

Pseudo total content of PTEs between the untreated tailings and those that were smouldered and roasted had shown some changes in composition. Some PTEs were reduced in concentration after smouldering and others increased (Table 5.1). Akatiti tailings copper content was reduced by 22% (6600 mg/kg) as compared to the untreated tailings (8500 mg/kg), which may be caused by the breakdown and volatilisation of copper during smouldering or may reflect inadequate correction for mass loss of the tailings during smouldering. No change in cobalt concentration (0%) and some decrease in phosphorus (1200 to 950 mg/kg; 21%) were also observed.

Table 5.1 Pseudo -total concentrations of PTEs for untreated, smouldered and roasted samples of Akatiti and Uchi tailings reported as mgkg-1 ± sd -dry tailings.

Element	**Untreated Akatiti tailings**	**Smouldered Akatiti tailings**	**Akatiti tailings @600 °C**	**Akatiti tailings @1000 °C**	**Untreated Uchi tailings**	**Smouldered Uchi tailings**	**Uchi tailings @600 °C**	**Uchi tailings @1000 °C**
Al	20000 ± 600	26800 ± 4900	22585 ± 0	23070 ± 810	10900 ± 470	16000 ± 1000	14336 ± 1373	36670 ± 1950
Ca	15400 ± 800	12200 ± 1600	11052 ± 1059	12275 ± 1080	60000 ± 1800	71700 ± 3700	62400 ± 6970	68776 ± 2820
Co	80 ± 2.0	80 ± 13	59 ± 0	50 ± 2.0	350 ± 12	410 ± 20	365 ± 29	390 ± 23
Cr	50 ± 2.0	70 ± 10	46 ± 1.0	49 ± 4.0	25 ± 1.0	40 ± 5	26 ± 2.0	49 ± 4.0
Cu	8500 ± 450	6600 ± 1100	7000 ± 330	5400 ± 280	6200 ± 74	6700 ± 400	5800 ± 550	5700 ± 170
Fe	25200 ± 900	40200 ± 12800	27648 ± 110	26337 ± 1646	15500 ± 440	40300 ± 16900	18386 ± 1730	21433 ± 700
K	14600 ± 600	20400 ± 3600	18124 ± 240	16850 ± 600	10000 ± 300	11300 ± 370	10494 ± 1120	23559 ± 1540
Mg	26900 ± 840	28200 ± 4500	27690 ± 240	26526 ± 2270	36100 ± 1200	43400 ± 2400	40949 ± 4700	46760 ± 2160
Na	700 ± 0.1	270 ± 0.1	210 ± 60	560 ± 11	68 ± 0.1	270 ± 0.1	138 ± 14	1600 ± 75
Ni	50 ± 4.0	60 ± 10	43 ± 1.0	37 ± 3	16 ± 1.0	30 ± 10	20 ± 2.0	23 ± 1.0
P	1200 ± 40	945 ± 180	810 ± 75	898 ± 60	700 ± 25	1100 ± 140	733 ± 50	780 ± 47
S	530 ± 70	955 ± 340	372 ± 19	595 ± 17	3300 ± 64	4100 ± 140	3920 ± 340	4900 ± 165
Zn	6.0 ± 3.0	50 ± 17	1.0 ± 0	1 ± 0	40 ± 10	50 ± 10	11 ± 9	13 ± 4.0

Uchi tailings behaved differently during smouldering regarding copper, cobalt and phosphorous. Copper increased by 7.5% from 6200 mg/kg to 6700 mg/kg; cobalt increased by 15% from 350 mg/kg-dry tailings to 410 mg/ kg -dry; and phosphorous increased by 36% from 700 mg/ kg to 1100 mg/ kg dry tailings (Table 5.1). These increases may indicate transformation or decomposition of the mineral compounds containing these or other elements in the tailings. There were changes in colour of the tailings after treatment from grey to reddish brown in both Akatiti and Uchi tailings, which may be due to the oxidation of iron from goethite to hematite (Goforth et al., 2005; Ketterings and Bigham, 2000) or other iron mineral transformations. Transformation of iron minerals may have been accompanied by other mineral transformations.

5.3.2.2 Roasted tailings

After roasting at 600 °C and 1000 °C, normalised total PTE content of Akatiti and Uchi tailings was compared to the pseudo total content of untreated and smouldered tailings (Table 5.1). Both Akatiti and Uchi tailings had less copper at 600 °C and 1000 °C. Treatment at 1000 °C via roasting in a muffle furnace saw a reduction in the copper content to 6900 mg/kg dry tailings for Akatiti (19% lower than untreated) and 5700 mg/kg dry tailings for Uchi (8% lower than untreated) even after correcting for mass loss of the tailings during roasting. Some variability may exist because of heterogeneity; however, all were decreased. These decreases suggest that some of the copper may have become volatile at 1000 °C and lost in the emissions. Some studies suggest that heavy metals including copper may escape into the atmosphere when exposed to higher temperatures while others remain in the treated material (Narodoslawsky and Obernberger, 1996). In addition, mineral compounds containing copper may have transformed into new mineral compounds which may be difficult to acid digest in determining the pseudo-total content. Visible residues remained after acid digestion of roasted tailings.

Ozer (2019) suggested that at temperatures above 500 °C, primary and secondary metal sulphates undergo further decomposition thereby causing a decrease in the extraction of the non-ferrous metals such as copper (Table 5.2). Mass losses were observed during roasting at 600 and 1000 °C and were more pronounced at 1000 °C in both tailings (Appendix I, Table 5.3). Mineralogy analysis for copper and copper-cobalt minerals by XRD was inconclusive (Chapter 4, Section 4.3.1); however, based on these differences, further analysis of tailings mineralogy would be beneficial.

Comparing the pseudo total content of PTEs after roasting at 600 °C and 1000 °C with smouldered tailings, Akatiti tailings had more copper in the roasted tailings at 600 °C (7000 mg/kg dry tailings) than the smouldered tailings (6500 mg/kg dry tailings) as well as 1000 °C roasted tailings (5400 mg/kg) (Table 5.1). On the other hand, Uchi tailings increased copper concentration after smouldering (6600 mg/kg dry tailings; 8% increase from untreated) and decreased slightly after roasting at 600 °C (5800 mg/kg dry tailings) and at 1000 °C (5700 mg/kg). These differences may reflect heterogeneity in copper distribution in tailings, a concentrating effect beyond what is captured in the mass loss correction (increases), and/or element mass losses due to heating (decreases). For cobalt there was no significant change in composition between the untreated Akatiti tailings and smouldered; however, some decrease was observed after roasting at 600 °C and 1000 °C (26% and 38% decreases, respectively). Cobalt may have become more volatile and lost in the emissions (Table 5.1). After smouldering and roasting Uchi tailings, there was more cobalt in the smouldered and roasted material than those before treatment (17%, 4.3%, and 11% for smouldered, 600 °C and 1000 °C, respectively) (Table 5.1), which may reflect heterogeneity, a concentrating effect, or both.

5.3.3 Changes to pH dependent availability after smouldering

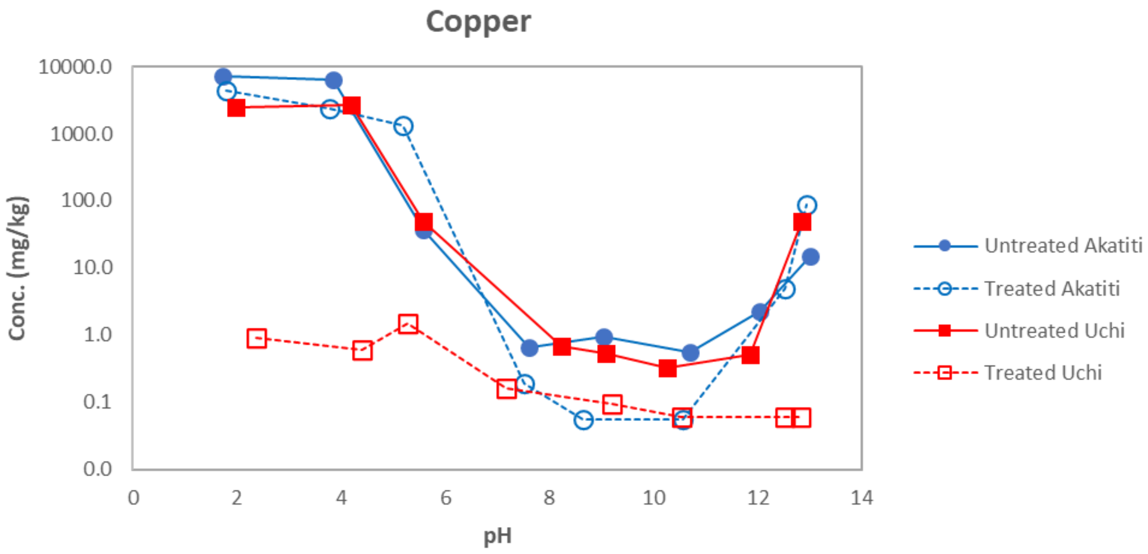
pH-dependent availability of copper and cobalt in untreated and smouldered tailings are presented in Figures 5.2 and 5.3. pH-dependent availabilities of other elements (Al, Ni, S and Zn) can be found in Appendix J. Copper in untreated Akatiti and Uchi tailings follows amphoteric availability profiles with elevated concentrations at $pH < 5.5$ and $pH > 10.5$ and low concentrations between these extremes. Cobalt follows cationic availability profiles with elevated concentrations at $pH \leq 5.5$. After smouldering, copper and cobalt availability profiles are different.

After smouldering, copper availability in Akatiti tailings remains amphoteric with some changes at different test positions. Reduced availability is observed at pH 2 compared to untreated tailings, with 2190 mg/kg available (26 %) compared to 7040 mg/kg (83 %) from untreated tailings. At pH 5.5, copper availability after smouldering is greater than availability in untreated tailings (1330 mg/kg (20 %) vs 37.55 mg/kg (0.4 %)), which may reflect some loss of buffering capacity. The cobalt availability profile seems to follow a similar pattern. After smouldering, cobalt availability seems weakly amphoteric. In the acidic range ($pH < 5.5$), cobalt availability is less than what was observed from untreated tailings while in the neutral to alkaline range ($5.5 \leq pH \leq 12$), cobalt concentration is low but greater than what was observed in untreated tailings. These results have important implications for recovery and remediation. Smouldering in these conditions does not enhance acidic recovery compared to recovery from untreated tailings and if recovery is not carried out, smouldered Akatiti tailings seem capable of releasing copper into the environment, perhaps sooner than untreated tailings, should acid mine drainage conditions develop.

Smouldering had different effects on Uchi tailings. Copper availability in Uchi tailings seems to follow a weakly cationic / weakly soluble profile after smouldering with all concentrations falling below those of untreated tailings. All copper concentrations in Uchi tailings across the full pH range fall below the EU and USEPA drinking water standards for copper (2.0 mg/L and

1.3 mg/L, respectively). The cobalt availability profile remains cationic with similar observation to smouldered Akatiti tailings. Cobalt availabilities are highest in acidic conditions (pH ≤ 5.5) but below cobalt availabilities in untreated tailings. In more alkaline conditions (pH > 9), cobalt availabilities in smouldered tailings exceed those in untreated tailings, although concentrations remain low overall (<1% pseudo-total content). Patterns for other PTEs in Akatiti and Uchi tailings vary, but generally, availabilities are lower compared to untreated tailings. Smouldering Uchi tailings does not enhance acidic recovery compared to recovery from untreated tailings; however, it seems to offer benefit for remediation, reducing copper and cobalt availabilities, as well as other PTEs, in neutral to acidic conditions compared to untreated tailings. The residue remaining after smouldering of tailings could be safe to be disposed or reused as a construction material since they do have much available copper or cobalt at 2 ≤ pH ≤ 13; however, based on poor recoveries of copper, other approaches that enhance copper recovery may be more desirable.

The lower amounts of copper available after smouldering compared to the untreated tailings, especially for Uchi, may reflect differences in mineralogy between Akatiti and Uchi tailings and changes in mineralogy during smouldering. Mineralogy characterisation showed different compositions to both tailings but did not identify copper or copper-cobalt minerals in either tailings source (Chapter 4, Section 4.3.1). The differing responses to heating via smouldering support further mineralogical and geochemical analysis. Smouldering is likely forming new mineral compounds in Uchi tailings that are more difficult to leach with acids or alkaline solutions. Lower leachability of heavy metals has been reported in other research on smouldering for combusted pulp and deinking paper (Kozinski and Zheng, 1999). The behaviour was linked to changes in the sample morphology of the burned material into a dense material causing fixation of the heavy metals within the alumino silicate matrix of residual ash. Smouldering of liquids does not leave behind residual ash, but the residual tailings composition may have analogous minerals. Further analysis on mineralogy and geochemistry of these tailings would be beneficial to understand these behaviours.



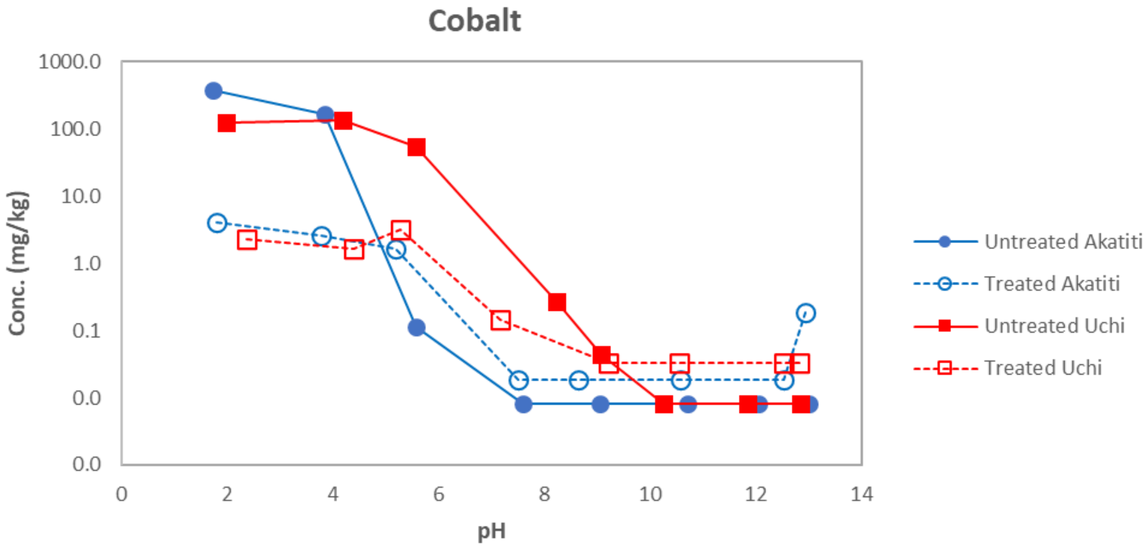


Figure 5.2 A comparison of USEPA Method 1313 pH-dependent availability of copper and cobalt before and after smouldering for Akatiti and Uchi copper mine tailings with a range of 2 ≤pH ≤ 13. Other PTEs are shown in Appendix J, Figure 7-J.

5.3.4 pH dependent availability from roasted tailings (2 ≤ pH ≤ 5.5)

Copper and cobalt recoveries after roasting were also examined focusing on the acidic range with highest availabilities in the untreated and smouldered tailings. Roasting tailings at 600 °C and 1000 °C changed the pH of the material from being mildly alkaline to strongly alkaline. Akatiti tailings changed from pH 8.5 to 12.8 (600 °C) and 10.6 (1000 °C). Lower pH of Akatiti tailings at 1000 °C may have occurred due to excessive mineral transformation leading to the reduction in the pH as compared to the pH attained after treating at 600 °C. Uchi tailings changed from pH 8.1 to 12.5 (600 °C) and 12.9 (1000 °C) (Table 5.2). In comparison, smouldering did not change pH much: 8.7 for Akatiti and 8.0 for Uchi.

Table 5.2 pH changes in the tailings before and after roasting and smouldering.

Treatment	**Akatiti tailings (pH)**	**Uchi tailings (pH)**
Untreated	8.5	8.1
600 °C	12.8	12.5
1000 °C	10.6	12.9
Smouldered	8.7	8.0

The availability of copper in Akatiti tailings after treatment at 600 °C was lower when compared to untreated tailings at pH 2 and pH 4 except at pH 5.5. Approximately 76%, 74% and 36% were extracted at pH 2, 4 and 5.5 respectively. Lower recovery was observed at pH 2 and pH 4 less than what was recovered from the untreated tailings (83% and 76% respectively). More copper was extracted at pH 5.5 after roasting at 600 °C (36%) when compared to the untreated tailings with 0.4%) (Figure 5.3). After treatment at 1000 °C, copper was made more immobile with only 4-5% available at pH ≤ 4 (Figure 5.3). Smouldering of Akatiti tailings yielded 67%, 35% and 20% available at pH 2, 4 and 5.5, respectively. Neither thermal treatment enhanced copper recovery from Akatiti tailings. Other PTEs such as cobalt (Figure 5.3), aluminium, iron, phosphorous and zinc (Appendix L, Figure 9-L) had reduced availabilities at pH ≤ 5.5 as well. Most of the copper in the untreated Akatiti tailings seems to be in oxide form (Chapter 4). As heating increases, PTEs seem to be stabilised in less mobile forms. Heating does not seem beneficial for enhancing copper or cobalt recovery. However, it helps reduce the availability of copper and cobalt at lower pH conditions (pH ≤ 4).

Treating Uchi tailings in the same conditions yielded different results, particularly at 600 °C. The amount of copper available in the eluate at pH 4 was improved to 63% when compared to 43% extraction before treatment. After treatment at 1000 °C, maximum copper availability decreased to 41% (pH = 2), similar to what was available before treatment. In comparison, smouldering reduced maximum copper availability to 0.01% (pH = 2). Higher availability of the copper after roasting at 600 °C may reflect oxidation of the copper sulfide minerals to acid soluble forms. Roasting at higher temperatures (and smouldering; Section 5.2.1) seems to cause further oxidation to insoluble forms. Based on these differences, the parent copper minerals in Uchi tailings are likely different from those in Akatiti tailings and further investigation of these mineralogy differences would be beneficial. Further testing varying low temperature roasting temperature would also be beneficial to optimise copper recovery via acidic extraction.

These findings suggest that treatability of the sulfide tailings by roasting and leaching depends on the tailings source (i.e., surface, or underground mining), how long they have been exposed to atmospheric (oxidative) conditions, and how much oxidation they have experienced. Differences likely extend to other tailings across the Zambian Copperbelt. Leaching alone may be enough to recover valuable copper and a combination of roasting and leaching may be required for others.

The cobalt recovery in both tailings (Akatiti and Uchi) after treatment did not improve, suggesting that further exploration of thermal treatments including smouldering and roasting would not be beneficial for enhancing cobalt extraction. Typical methods for cobalt extraction involve stronger acid extraction than the Method 1313 pH range and subsequent separation from other impurities such as aluminium, iron. manganese and copper. The high-quality cobalt hydroxide that is recovered (Fisher and Treadgold, 2009) can be redissolved and used in producing pure cobalt metal via electrolytic deposition (Crundwell et al., 2020).

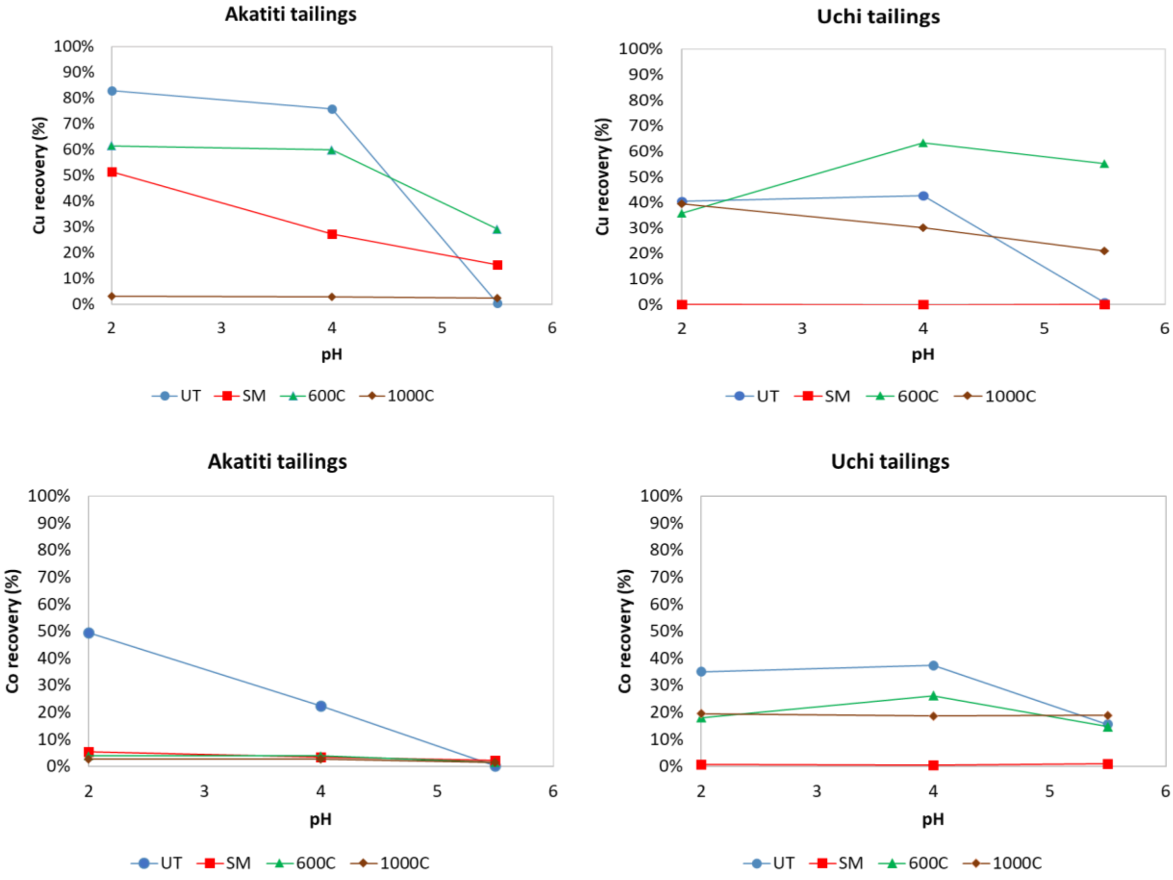


Figure 5.3 Recovery of copper and cobalt using a pH dependence leaching test method at targeted pH values of 2,4 and 5 for the untreated, smouldered, and roasted temperatures. The leaching graphs of phosphorous and sulfur are presented in Appendix L, Figure 9-L).

5.3.5 Column leaching results for smouldered Akatiti and Uchi tailings

Examining dynamic leaching, smouldered tailings released slightly more copper and cobalt compared to untreated tailings (Figure 5.4). Cumulative releases were low (<1 mg/kg) for all materials. There was an early washout of copper and cobalt with maximum releases at liquid to solid ratio of 2 and then decreasing after this point, reflecting availability-controlled leaching. The relative increased washout from smouldered tailings cannot be explained by pH changes compared to untreated tailings. These differences were small. Instead, increased washout likely reflects a loss in buffering capacity during smouldering.

Sulfur exhibited an increase in leaching from Akatiti tailings and a reduction in leaching from Uchi tailings after smouldering (Figure 5.4). Cumulative releases of sulfur were higher than releases of other elements, which may reflect the capacity of tailings to generate acid mine drainage conditions that have affected similar areas of the Copperbelt (Kosgei et al., 2020). The increase in sulfur release from Akatiti tailings comprises 33% of total sulfur and most of this release was an early washout occurring before L/S = 2. In contrast, untreated Akatiti tailings released little sulfur early on but experienced sustained slow release across the full L/S range. Changes to initial pH were small and likely had little influence on this difference. Akatiti tailings may have undergone further oxidation from smouldering, triggering increased release of sulfur. This is interesting because these tailings are already weathered and oxidised (Chapter 4). Untreated and smouldered Akatiti tailings experience little change in sulfur availability across the full L/S range, Figure 5.4). In contrast, cumulative sulfur released from smouldered Uchi tailings was significantly lower than that of the untreated tailings, which was expected based on the Method 1313 results (Section 5.3.3). The treatment of copper tailings via smouldering for Uchi tailings has potential of reducing the sulfur concentration and thus potentially reducing the dissolution of other potentially toxic elements such as copper and cobalt, among others. In addition, reduction in the cumulative release of sulfur can reduce the occurrence of acid mine drainage because it has potential of reducing the formation of sulphates. Cumulative releases of other PTEs such as aluminium, iron, potassium, magnesium, sodium, nickel, phosphorous and zinc are presented in Appendix K, Figure 8-K cumulative releases were all low.

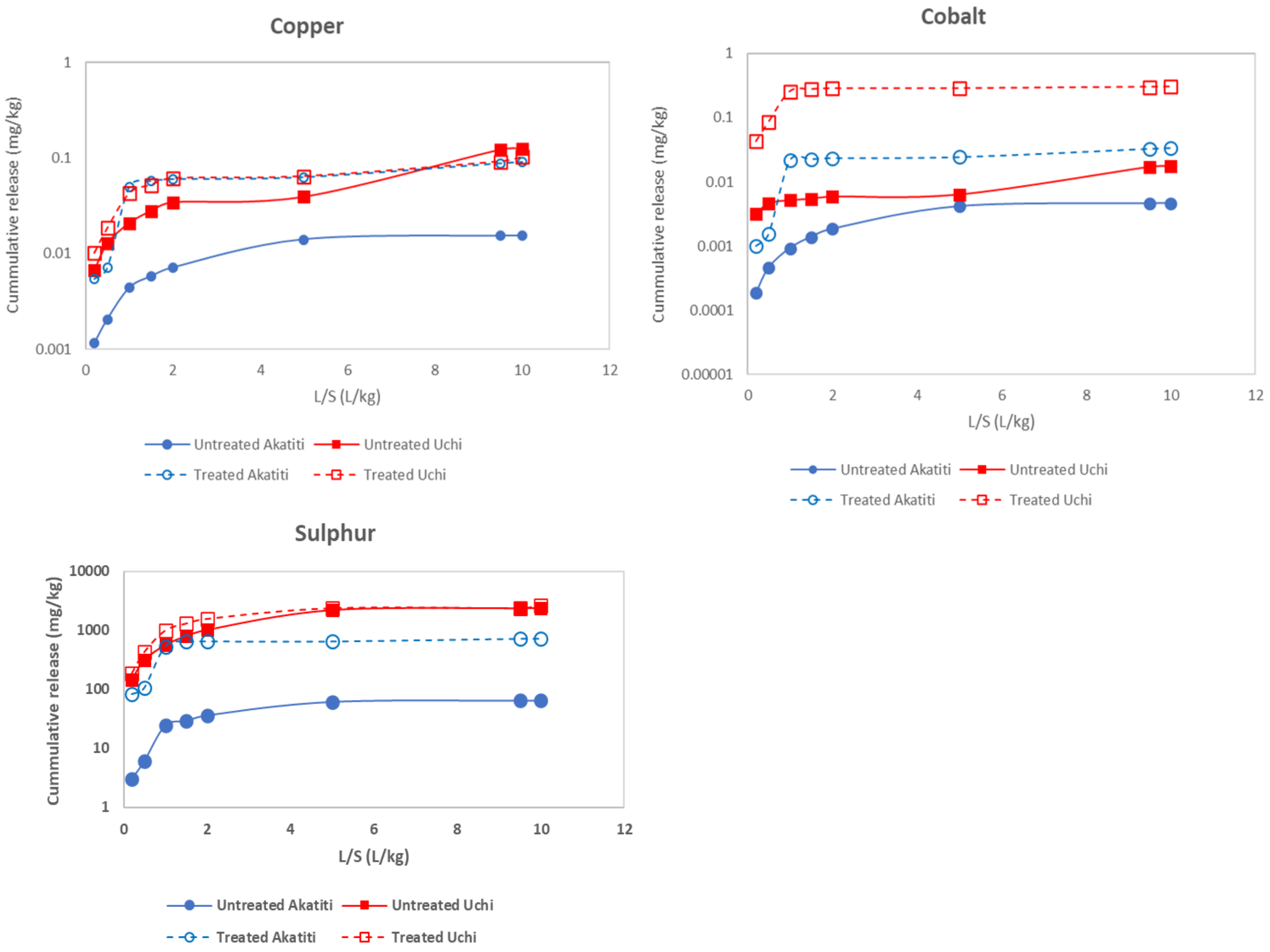


Figure 5.4 Cumulative releases of copper, cobalt and sulfur from a percolation column leaching experiment for smouldered and untreated Akatiti (AT) and Uchi (UT) tailings. Other PTEs (Al, Fe, K, Mg, Na, Ni, P, and Zn) are presented in Appendix K, Figure 8-K.

5.3.6 Discussion: comparing smouldering and roasting

There are some notable similarities and differences observed between smouldering and roasting. Smouldering was applied with the notion that it may be a substitution for roasting because of its self-sustainable energy; however, the average peak temperatures reached were possibly too high and this may have caused some PTE volatility and changes in mineralogy. These changes resulted in lower extraction efficiencies for copper, cobalt, and other PTEs, especially at low pH (≤4), which is a plus for environmental remediation but does not facilitate efficient recovery of copper or cobalt. Comparing the two treatment methods with the untreated tailings, neither smouldering nor roasting are improving the extraction efficiency of copper for mineral resource recovery to a larger extent except for Uchi tailings at 600 °C roasting. It seems better to directly leach the Akatiti tailings without any exposure to heat to avoid potentially unnecessary energy costs. Further exploration of the lower temperature range (i.e., around, or below 600 °C) or reducing the roasting time (or both) may be beneficial for enhancing copper recovery from Uchi tailings; however, exploration of stronger acidic extractions may be more cost effective instead. To achieve a single remediation objective of PTE immobility, tailings can be subjected to heat treatment either via smouldering or roasting at higher temperatures.

5.4 CONCLUSIONS

Smouldering and roasting treatments had differing effects on Akatiti and Uchi tailings. Reduction in total copper (22%) was observed in the smouldered Akatiti tailings and no change was observed in total cobalt (0%). Uchi tailings behaved differently after smouldering. Copper and cobalt contents were unaffected, experiencing a small concentrating effect due to mass loss from the tailings. pH dependent availabilities of copper and cobalt were different as well.

Collectively, these changes may reflect mineral transformations and/or decomposition as well as mineral differences between Akatiti and Uchi tailings, which would make sense given their different origins. The application of roasting at 600 °C for Uchi tailings improves the extraction efficiency of copper from 43% to 63% compared with the untreated tailings; further exploration of low temperature roasting may yield further recovery from Uchi tailings. Direct leaching may be a more appropriate method to recover copper and cobalt to avoid additional energy costs and reduce possible emissions from volatile compounds. To achieve a single remediation objective of PTE immobility, heat treatment of tailings via smouldering or roasting at higher temperatures has some benefit.

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6.0 CHAPTER 6 – SOIL WASHING RECOVERY AND REMEDIATION OF COPPER MINE TAILINGS.

ABSTRACT

This study investigates the recovery and remediation potential of copper and cobalt from copper mine tailings from the Zambian Copperbelt using an acid washing process. Washing copper tailings with 0.5M HCl for 24 hours extracted 82 - 100% of copper and 8 – 36% of cobalt. Reducing the wash time to 4 hours reduced extraction efficiency for copper to 58 – 79% and increased for cobalt to 55% for cobalt which are similar with those observed at pH 2 for 24 hours in Method 1313 (Chapter 4). The longer wash period at pH 0.3 removes copper in most of the tailings to levels below the Dutch Screening Values for soil. Soil washing with concentrated hydrochloric acid shows promise to increase the extraction efficiency of copper and cobalt to achieve soil remediation while recovering the mineral resource. The efficiencies of other acids should also be examined to compare with hydrochloric acid to optimise copper recovery. Additional work with stronger acid concentrations may be beneficial to improve cobalt recovery.

Keywords: Potentially toxic elements; soil washing; extraction; mineral resource; copper; remediation

6.1 INTRODUCTION

Mining activities generate large amounts of waste in various forms including waste rocks, overburden materials, tailings, and slag. Mine wastes contain potentially toxic elements (PTEs) in various forms such as oxides, carbonates or sulfides that influence their reactivity, mobility, and bioavailability (Yobouet et al., 2010). Metals and metalloids resulting from mining activities such as copper, lead and zinc mining can contaminate the surrounding soils and ground and surface waters. Once PTEs are available in the soils, they are not biodegradable by natural processes and remain in the environment (Kedziorek and Bourg, 1999).

Copper is used as an active ingredient for biocides and is reported as one of the most toxic elements to soil microorganisms and therefore soil health (Borkow and Gabbay, 2005; Dussault et al., 2008). The environmental impact of copper is mostly from its mobility into the surrounding water or uptake by plants (Onweremadu and Duruigbo, 2007). Various treatment methods for PTE-contaminated soils exist such as chemical treatment, bioremediation and phytoremediation that transform PTEs into less available and/or less harmful forms (Mulligan et al., 2001). Other methods including back filling and solidification immobilise PTEs in place. All have short comings including inability to achieve concentration reduction or complete clean-up of the soil (Chapter 2).

Soil washing is an ex-situ remediation process that uses combined techniques of physical separation and aqueous solutions to reduce the concentration of contaminants (William,1993). Soil washing is one of the few remediation processes that can achieve concentration reductions of PTEs. During the washing process, contaminants are removed from the soil matrix by dissolving them in a washing solution (Peters, 1999). Soil washing is an effective method of contaminant removal (Cao et al., 2009 and Yobouet et al., 2010). After treatment, cleaned soil may be suitable for reuse (Liu et al., 2010) subject to local legislation and policy.

Soil washing is an effective technology to remove potentially toxic elements in a short period of time (Damont et al., 2008; Yang et al., 2009). Factors that govern the removal efficiency of PTEs include soil or waste characteristics; the chemistry of the extractant; and the contaminant characteristics in the soil or waste material (Mann, 1999).

In Chapter 4, copper and cobalt were identified as mineral resources of value that can be recovered as part of a remediation strategy. The pH-dependent availability test (Method 1313) showed that much of the copper was available in the extracts at pH < 4 although this extraction did not remove enough copper or cobalt to achieve levels that fall below the Dutch Screening Values for soils (Table 4.2, Chapter 4). Thermal treatment had limited effects on copper and cobalt extractability (Chapter 5). Tailings seemed to have varying mineralogies based on copper and cobalt recoveries as well as responses to thermal treatment, although XRD testing was inconclusive (Chapter 4). Three possible approaches may increase recovery via acidic extraction: reducing the pH of extraction, increasing the liquid to solid ratio (L/S) of extraction, and varying the acid used for extract. This study examines the influence of reducing extraction pH.

6.2 MATERIALS AND METHODS

Tailings from Akatiti, Kitwe, and Uchi tailings dams in the Zambian Copperbelt (Chapter 4) were used in this study. Samples were prepared by air drying to remove the moisture content in the tailings prior to washing. After drying, the material was sieved using the 2 mm sieve size to remove all the extraneous materials and stored at 4 °C until its use.

Soil washing was conducted using 0.5M of hydrochloric acid (pH < 1) for 4 hours and 24 hours contact times. The liquid to solid ratio was 10. Each sample mass of 3 grams was weighed into a 100 mL polythene bottle and 30 mL of the 0.5 M of HCl was added as a washing solution. The prepared extraction bottles containing the two materials (HCl solution and tailings) were sealed and shaken end-over-end for 4 or 24 hours at 120 RPM. After shaking, bottles were then left to stand for 10 minutes, and the leachate was filtered using 0.45 µm filter membrane (Whatman, PTFE In-line Filter 0.45 Micron) to remove suspended solids. Filtrates were transferred to 10 ml centrifuge tubes and preserved by adding a drop of concentrated nitric acid. Samples were stored at 4 °C until chemical analysis. Filtrates were analysed for PTEs by ICP-OES (iCAP 6200, Thermo Scientific; 50 RPM analysis pump rate, 1150W RF power; and 5s pump relaxation time) following the method used previously (Chapters 4 and 5). PTE results were normalised by moisture content of the original tailings and the results are presented as mg/kg-dry tailings, the same approach as used in Chapters 4 and 5.

6.3 RESULTS AND DISCUSSION

6.3.1 Physical and chemical characteristics

Tailings have organic content of $\leq 0.8\%$ with a pH ranging from neutral to mildly alkaline ($7.2 \leq pH \leq 8.5$) (Table 4.1). The tailings contain high levels of copper (0.45 – 0.85 %) and cobalt (0.016 – 0.049 %) (Chapter 4) that can be considered as mineral resources (Limpitlaw, 1998; Seecharan, 2013). In mild acidic solutions ($2 < pH < 4$), 83 %, 73 %, and 43 % of copper and 49%, 16%, and 36% of cobalt can be recovered from Akatiti, Kitwe, and Uchi tailings, respectively (Chapter 4).

6.3.2. Copper and cobalt recoveries with acid washing

With 24 hours washing time in 0.5 M HCl, 94% of copper was recovered from Akatiti tailings, effectively 100% from Kitwe tailings, and 82% from Uchi tailings (Table 6.1). With 4 hours washing time, 0.5 M HCl was able to extract 62%, 79% and 58% for Akatiti, Kitwe and Uchi tailings, respectively. The extraction of copper using 0.5 M of hydrochloric acid (HCl) had shown similar extraction efficiencies at 4 hours with those observed after 24 hours extraction with ~0.01M nitric acid (pH 2) (Chapter 4), which leaves concentrations of copper in all tailings above the Dutch screening values for soil (190 mg/kg). At 24 hours washing time, copper levels in Kitwe tailings fell below this value, as well as the target value (0.3 mg/kg), which shows the importance of contact time and the difficulty of achieving enough reduction. Both Akatiti (94% recovery) and Uchi tailings (82% recovery) still exceeded these screening values; Akatiti would require 98% recovery and Uchi would require 97% recovery. With the relatively small sample sizes (3 g) and potential for variability across the tailings, copper recoveries will likely vary, too, which further illustrates the challenge.

Cobalt recoveries with 4 and 24 hours of acid washing followed different patterns to copper recoveries (Table 6.1). Akatiti tailings did not contain much cobalt and recoveries were low (6 and 8% at 4 and 24 hours washing period respectively). Both Kitwe and Uchi tailings showed more cobalt recovery after 4 hours than 24 hours, but all recoveries were < 60%. In contrast to copper recoveries, cobalt recoveries from Uchi tailings left the extracted tailings below the Dutch Screening intervention value for soil (190 mg/kg) after either extraction time (55% and 36% at 4 and 24 hours respectively); however, neither achieved the target value (190 mg/kg). Extractions from Kitwe tailings did not achieve either intervention or target values. Akatiti tailings already fell below the intervention value.

Hydrochloric acid has been recognised as one of the extractants that is able to mobilise PTEs in soils by decomposing mineral compounds that may be present in the soil matrix (Ke et al., 2004). The differing extraction recoveries for copper and cobalt may reflect differences in sorbed and mineral copper and cobalt forms among the three tailings sources, including the different parent ores in Luanshya (Akatiti) and Kitwe (Kitwe and Uchi). In Chapter 4, XRD results do not show the prevalent presence of copper minerals despite elevated levels of copper in the pseudo-total contents of the tailings (Tables 4.1 and 4.3). Mineral formations present in higher quantities for Akatiti tailings include Mica (bornite and muscovite; 37%) and K-Feldspar (44%) as the main mineralogical compositions. In Kitwe tailings, dolomite (19%)

and quartz (18%) are more prevalent. In Uchi tailings K-Feldspar (31%) and Mica (bornite and muscovite; 16%) are more prevalent (Table 4.3). Based on the different recoveries here and differing responses to thermal treatment (Chapter 5), this calls for further analysis to have a deeper mineralogical characterisation and differentiate between mineral and sorbed forms of copper.

6.3.3 Neutralisation of tailings residues after acid wash

The residues remaining from acid wash of the tailings to recover the copper and cobalt can be neutralised by adding lime (calcium oxide or calcium hydroxide) to control the pH from being too acidic to neutral so that further leaching of other PTEs in the tailings residue can be minimised. Lime addition is considered as the most effective and economic pH modifier that is used to achieve selective flotation of minerals in sulfide ores (Zanin et al., 2019).

Table 6.1 Soil washing results of PTEs at 4 and 24 hours washing period in mg/kg-dry tailings using 0.5M HCl.

Elements	**Untreated Akatiti tailings**	**Akatiti 4 hours acid wash**	**Akatiti 24 hours acid wash**	**Untreated Kitwe tailings**	**Kitwe 4 hours acid wash**	**Kitwe 24 hours acid wash**	**Untreated Uchi tailings**	**Uchi 4 hours acid wash**	**Uchi 24 hours acid wash**
Al	19900	880	950	13600	240	310	10800	240	320
Ca	15300	6910	10700	60700	49340	45740	60000	48150	47650
Co	76	4.6 (6.1%)	6.0 (7.9%)	517	190 (37%)	120 (23%)	350	190 (55%)	124.9 (36%)
Cr	49	1.6	1.6	30	0.1	0.1	25	0.1	0.1
Cu	8500	5260 (62%)	8000 (94%)	4480	3600 (80%)	5070 (113%)	6200	3620 (58.5%)	5077.2 (82%)
Fe	25100	2200	2920	15500	2180	2710	15400	2340	2890
K	14500	970	970	11500	1350	1158	10100	1300	1280
Mg	26800	3370	4700	39500	14130	13810	36000	14000	14130
Na	675	10.5	7.5	54	21.5	16.5	68	22.9	16.4
Ni	48	1.9	2.2	18	1.7	2.1	16	1.7	2.0
P	1200	470	730	700	0.5	1.0	700	1.2	0.4
S	530	420 (79%)	640 (120%)	2400	1800	2980	3300	1780	2940
Zn	6.3	17.3	34.0	20	31.1	4.3	20.4	28.0	4.9

6.4 DISCUSSION

Soil washing with a highly concentrated hydrochloric acid of pH 0.3 has shown potential of increasing the extraction efficiency of copper (82-100%) and cobalt (5-55%) from copper mine tailings. This process achieves some remediation while recovering copper and some cobalt. Direct leaching of the tailings can be applied without pre-treatment of the tailings by thermal methods (e.g., roasting or smouldering), which saves on energy costs. Reducing the pH of the leaching solution from 2 to 0.3 and using a 24-hour washing period has played a significant role in achieving higher extraction efficiencies. In Akatiti tailings, copper recovery increased from 83% (Chapter 4) to 94%, Kitwe tailings from 73% to 100% and Uchi tailings from 43% to 82%. Cobalt yields improved less and were from the 4-hour wash period. Further reduction in solution pH should yield more recovery. In addition, other options such as increasing the L/S ratio above 10, reducing the pH of the leaching solution, and use of other acids such as sulfuric acid should be investigated and possibly combined to maximise the recovery potential of copper and cobalt. Economic analysis should also factor into this investigation. For example, sulfuric acid is one of the readily available acids in Zambia because it is easily produced from the smelting process of sulfide minerals. It may be more advantageous as extraction solvent in comparison to something else that has to be imported. In the case of the tailings studied here, recovery is remediation. The concentrations of other contaminants of potential concern are all below levels of concern (Chapter 4). Focusing on copper and cobalt recovery has the potential to achieve both economic and environmental objectives simultaneously.

6.5 CONCLUSION

Soil washing with 0.5 M hydrochloric acid was applied with the aim of increasing the extraction efficiencies of copper and cobalt from copper mine tailings and reducing residual concentrations in the tailings to safe levels. Copper extraction efficiencies improved to 82 – 100% with 0.5 M hydrochloric acid from 43 - 83% with 0.01 M nitric acid with a 24-hour washing period. Extraction efficiencies varied by tailings source, suggesting mineralogical differences between the materials. The 24-hour washing period was important. Copper recoveries after 4 hours of washing were 59 - 80%, similar to those observed with the weaker nitric acid extractions. Extractions reduced the amount of copper remaining in the tailings and brought one of the three tailings sites below the Dutch Screening Value for copper in soil. Cobalt recovery and remediation in Kitwe and Uchi tailings did not improve as much with the stronger hydrochloric acid and the 4-hr washing period was slightly more efficient than the 24-hr washing period. Extraction reduced the cobalt concentration below the Dutch Screening Value for cobalt in soil in Uchi tailings, but not enough to achieve the target value. Extraction leaves Kitwe tailings above the screening value. Akatiti tailings do not have much cobalt and are already below the screening value. Further work exploring other acids concentrations, and increased L/S would be beneficial to maximise copper recovery from tailings. Other recovery methods, likely with stronger acid concentrations, may be needed for cobalt. Based on this work, resource recovery and remediation can be achieved at the same time.

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7.0 CHAPTER 7 – CONCLUSIONS, FUTURE WORKS, AND RECOMMENDATIONS

7.1 Conclusions

Akatiti, Kitwe and Uchi copper mine tailings from the Zambian Copperbelt have elevated levels of copper present that can be regarded as ore in other regions. Copper concentrations in tailings were 43 – 83%. Scaling those figures, 550 000 tonnes of copper may be recoverable from these three tailings dams and 6.8M tonnes of copper from Zambia's estimated 791M tonnes of copper mine tailings countrywide.

Elevated levels of cobalt are also present in Kitwe and Uchi tailings (350 – 510 mg/kg) while smaller quantities are present in Akatiti tailings (76 mg/kg). The levels at Kitwe and Uchi are below what would be considered cobalt ore in other countries; however, they are comparable to levels that are recovered as copper-cobalt ores.

The presence of elevated levels of copper in the underlying soils at Kitwe and Uchi indicates that some PTE mobility of copper may have occurred through acid mine drainage. Elevated concentrations of copper, cobalt and sulfur, possible washout from the tailings, have been reported in nearby streams and rivers which indicates possible acid mine drainage is taking place. Zambia's 791M tonnes of copper mine tailings represent large stockpiles of copper, cobalt, and sulfur for further release. For these reasons, remediation is urgently needed.

Simultaneous remediation and recovery of copper and, to a lesser extent, cobalt is possible by acid washing. Extraction with 0.01M nitric acid yielded 43 – 83% removal of copper and 16 – 49% of cobalt. Extraction efficiencies improved to 82 -100% copper (24-hour extraction) and 5 -53% cobalt (4-hour extraction) with 0.5M hydrochloric acid. Efficiencies varied by tailings source. Stronger acid extractions can further improve efficiency. Other stronger acid concentration should be explored which can help increase the extraction potential of cobalt such as sulfuric acid since it is produced locally in Zambia.

Although extraction efficiencies for copper were as high as 82 – 100%, the strongest extraction conditions studied here (0.5M hydrochloric acid) only achieved sufficient copper removal from Akatiti and Kitwe tailings and sufficient cobalt removal from Kitwe and Uchi tailings to fall below the Dutch Screening Values for soil, which shows difficult in achieving full remediation.

Roasting the tailings at 600 °C had a benefit of increasing the extraction efficiency of copper for Uchi tailings from 43 to 63%. Reduced availability from Akatiti tailings was also observed. On the other hand, smouldering the tailings before acid wash had no benefit of increasing the recovery potential and reduced the total copper content by 22% for Akatiti tailings. However, smouldering had the advantage of reducing PTE availability and leaching even at very low pH conditions (pH ≤ 4).

To maximise copper and cobalt recovery from Akatiti and Kitwe tailings, and others like them, direct acid leaching of the tailings should be applied without pre-treatment via smouldering or roasting. A 24-hour washing period, or possibly longer, should be considered vital to achieve efficient copper recoveries. Thermal pre-treatment of Uchi tailings, and others like it, should be explored further to optimise the conditions for copper recovery.

Mineral differences were apparent between Akatiti, Kitwe and Uchi tailings. XRD analysis did not show the presence of any copper or copper-cobalt minerals even though high levels of copper and cobalt were measured in the tailings. Differences in the total cobalt and sulfur highlight the differences in the origin of the orebodies between the three tailings sites. Further mineralogical characterisation of the tailings would be beneficial to differentiate between mineral and sorbed forms of copper and tailor remediation and recovery efforts to suit those characteristics.

This work has demonstrated that recovery of copper and some cobalt is possible as part of remediation which is urgently needed to protect water resources and the environment. The potential value of the tailings may offset the cost of remediation and may be profitable as well.

7.2 Recommendations for remining of copper tailings in Zambia

Close to 800M tonnes of copper mine tailings exist in Zambia covering around 10 000 hectares of land. Remining of copper is possible and about 6.8M tonnes could be extracted from the estimated copper tailings countrywide. However, an economic analysis of the total profits that could be generated from remining the copper and cobalt minerals from the tailings would be beneficial to understand the initial capital of investment for resource recovery and remediation.

Copper mine tailings contain very low levels of Cd, Cr, Pb and Zn, which likely simplifies the pollution problem and recovery efforts for the copper and cobalt minerals. Recovery of cobalt is possible in Kitwe and Uchi tailings. Remining the tailings and some of the bottom soils of Kitwe and Uchi tailings dams could save mining companies on blasting operations and cummunition processes compared to mining from the intact rock. This will potentially increase the employment levels for people in the areas these tailings are located.

Resource recovery of copper and cobalt can be achieved by direct leaching of the tailings without pre-treatment (for Akatiti and Kitwe tailings) using a concentrated acid wash such as hydrochloric acid or probably sulfuric acid, which is readily available in Zambia. Recovery of copper from Uchi tailings can be enhanced by gentle roasting before acid washing. Roasting the tailings at 600 °C improved the extraction potential from 43 to 63% and further enhancement is likely possible by optimising the roasting conditions.

Recovering the copper and cobalt has environmental benefit alongside its commercial benefit in protecting surrounding water bodies. Remining can help achieve the Zambian Government’s 2030 national vision to provide safe water to the people of Zambia as well as creating jobs for local communities.

Apart from the copper, these tailings (Akatiti, Kitwe and Uchi) have significant levels of aluminium that may be worth recovering, too. For example, aluminium recovery can be explored for aluminium cables production because of their corrosive resistant oxide layer properties. Increased aluminium production through remining could help expand on the current exports of these cables to Sub-Saharan African countries such as Botswana, Kenya, Malawi, Namibia, and Tanzania.

7.3 Recommendations for future research

Further characterisation of the mineralogy of the parent tailings and their underlying bottom soil is important to link tailings source to recovery options. Thermal treatment may help with that characterisation. Analysis using a scanning electron microscopy (SEM) to identify the mineral forms copper and cobalt is attached to and understand mineral transformation after treatment. Alternatively, XRD analysis can be repeated with additional beneficiation steps to concentrate the copper and cobalt minerals.

More exploration of thermal treatments including roasting and smouldering needs to be explored to facilitate increase in the extraction potential of the copper and cobalt minerals from tailings that are resistant to acid leaching. Pyrometallurgical methods may also be appropriate for some tailings.

Thermal treatment of the tailings via smouldering using vegetable oil as a fuel before leaching reduced the extraction potential of the copper and cobalt making them less mobile even at low pH conditions. This may have been caused by the high temperatures reached during treatment. Because roasting at 600 °C improved recovery from Uchi tailings, smouldering at lower temperature may have benefit as well. Low energy fuels such as biosolids should be explored to reduce the temperature of treatment to around 400 °C which may be favourable in achieving better extraction efficiencies and be an alternative to roasting because of its self-sustainability energy.

Furthermore, a laboratory beneficiation process can be setup at laboratory scale to evaluate the electroplating potential of the copper in the leached solution after acid wash via the electrowinning process. This will help calculate the costs of remediation via resource recovery. The generated copper cathodes from the electrowinning process at a large scale can be sold to companies producing final products of copper such as electrical cables for electricity supplies and those producing electrical vehicles for the greener economy.

The examination of Akatiti, Kitwe and Uchi tailings dams does not fully answer the recovery potential of copper and cobalt minerals in Zambia as this only represents three tailings' sites out of 45 known tailings dams in the Copperbelt region. For this reason, other tailings in the

Copperbelt need to be investigated so that a comprehensive resource recovery and remediation strategy can be developed countrywide.

8.0 Appendices: Supplementary Information for Chapter 4

COPPER AVAILABILITY AND MOBILITY FROM HISTORIC TAILINGS SITES IN ZAMBIA.

8.1 APPENDIX A: Geographical location of the sampling sites on the Copperbelt region and the sampling techniques used.

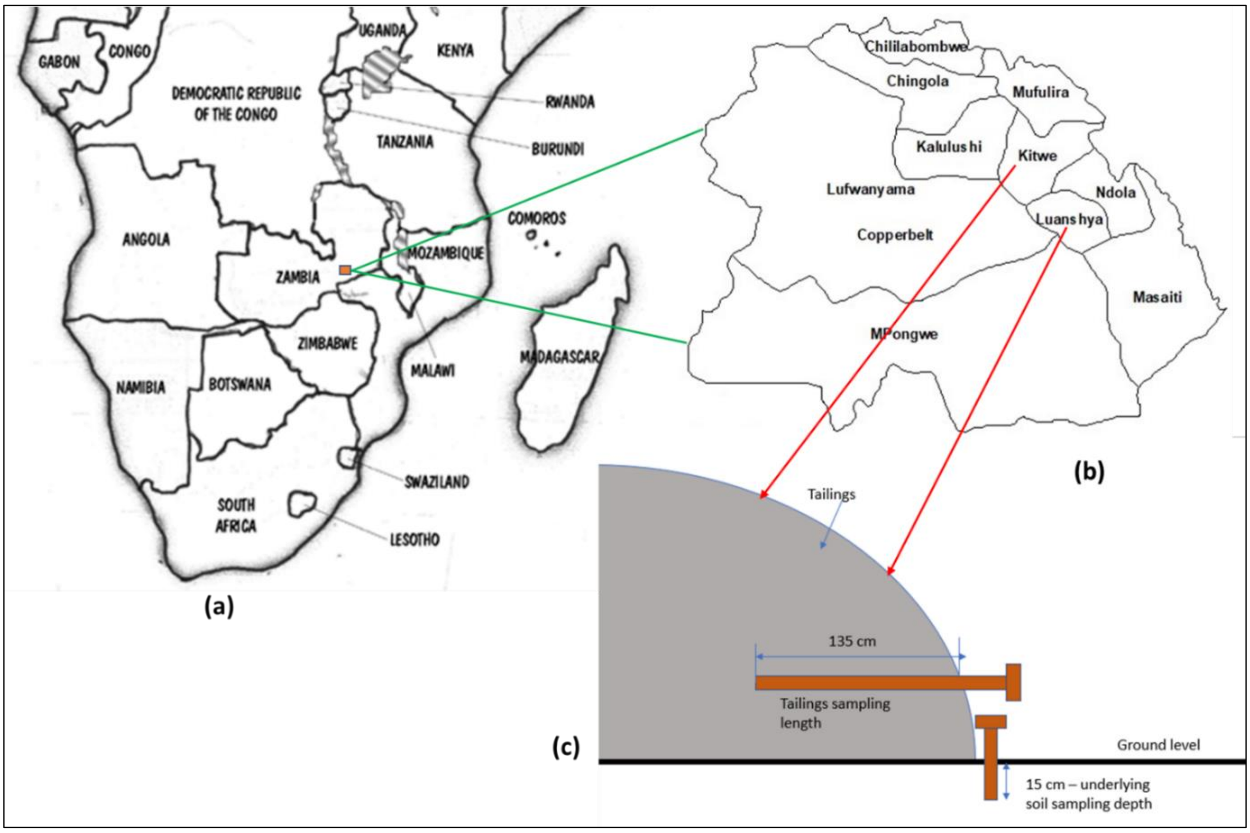

Fig. 1-A. Geographical location of Kitwe and Luanshya towns on the Zambian Copperbelt extracted from ArcGIS (b) and an illustration of sampling using a hand auger through the tailings and its underlying material (c) (Not drawn to scale).

8.2 APPENDIX B: Differences between bottom soil and tailings material

Table 3. Summary of the PTEs differences between the tailings and their underlying bottom soil.

Element	Akatiti	Kitwe	Uchi
Al	Elevated. Soil > tailings	Elevated. No significant difference.	Elevated. No difference
As	Elevated. Tailings > soil	Low. No significant difference	Low. No significant difference
Ca	Elevated. Tailings > soil	Elevated. No significant difference	No difference
Cd	Low. No significant difference	Low. No difference	Low. No difference
Co	Low. Tailings > soil	Elevated. No difference. Good opportunity for recovery.	Elevated. No difference. Good opportunity for recovery.
Cu	Elevated. Tailings > soil. Highest concentration. Good opportunity for recovery.	Elevated. No difference, Good opportunity for recovery.	Elevated. No difference. Good opportunity for recovery.
Cr	Soil > tailings	No difference	No difference
Fe	Soil > tailings	Tailings > soil	Tailings > soil
K	Tailings > soil	Tailings > soil	No difference
Mg	Tailings > soil	Tailings > soil	Tailings > soil
Na	Tailings > soil	Tailings > soil	Tailings > soil
Ni	No difference	No difference	No difference
P	Tailings > soil	Soil > tailings but not by a lot.	No difference

Pb	Soil > tailings	No difference	No difference. Highest Pb. Still very low.
S	Tailings > soil. Lowest S content of the 3 sites. Some soil acidification may have taken place.	Tailings > soil. Highest S content of the 3 sites. Some soil acidification may have taken place.	Soil > tailings. Soil acidification may have taken place, perhaps more than other sites.
Zn	Soil > tailings	No difference	No difference

8.3 APPENDIX C: Distinct leaching patterns of potentially toxic elements

Table 4. Three distinct leaching patterns exhibited by PTEs of Akatiti, Kitwe and Uchi tailings and their underlying bottom soils.

Elements	**Akatiti tailings**	**Akatiti soil**	**Kitwe tailings**	**Kitwe soil**	**Uchi tailings**	**Uchi soil**
Al	Amphoteric	Amphoteric	Cationic	Cationic	Amphoteric	Amphoteric
Ca	Cationic	Cationic	Cationic	Cationic	Cationic	Cationic
Co	Cationic	Cationic	Cationic	Cationic	Cationic	Cationic
Cu	Amphoteric	Amphoteric	Amphoteric	Amphoteric	Amphoteric	Amphoteric
Fe	Amphoteric	Amphoteric	Cationic	Cationic	Amphoteric	Amphoteric
K	Amphoteric	Amphoteric	Amphoteric	Amphoteric	Amphoteric	Amphoteric
Mg	Cationic	Cationic	Cationic	Cationic	Cationic	Cationic
Ni	Amphoteric	Amphoteric	Cationic	Cationic	Amphoteric	Cationic
P	Amphoteric	Amphoteric	Cationic	Cationic	Amphoteric	Amphoteric
Na	Amphoteric	Amphoteric	Amphoteric	Amphoteric	Amphoteric	Amphoteric
S	Highly soluble	Highly soluble	Cationic	Cationic	Highly soluble	Highly soluble
Zn	Amphoteric	Amphoteric	Cationic	Cationic	Amphoteric	Amphoteric

8.5 Appendix E: pH and Ec values for tailings after column leaching experiment

Table 5: pH and Ec values for Akatiti, Kitwe and Uchi tailings after column leaching experiment at different L/S ratios.

L/S	**Akatiti tailings**		**Kitwe tailings**		**Uchi tailings**	
	pH	Ec (Us/cm)	pH	Ec (Us/cm)	pH	Ec (Us/cm)
0.2	6.62	498	6.89	2290	6.29	3730
0.5	6.82	543	6.68	1940	6.39	2770
1	6.99	669	6.87	2060	6.67	2320
1.5	7.76	319	6.82	1482	6.79	2280
2	6.81	338	6.88	837	6.79	2240
4.5	6.64	346	6.85	1573	6.52	2310
5	6.81	589	6.9	538	7.07	1668
9.5	6.4	2380	6.36	452	6.41	838
10	6.81	542	6.92	431	7.05	1040

8.6 APPENDIX F: Extracted PTEs at pH 4 for the tailings

Table 6: Recovery of PTEs at pH 4 for Akatiti, Kitwe and Uchi tailings in mg/kg-dry

pH	Element	Akatiti tailings	Kitwe tailings	Uchi tailings
pH 4	Al	3240	64	180
	Ca	350000	22000	30640
	Co	17.0	82.0	130
	Cu	6450	3250	2630
	K	32400	1020	1400
	Mg	79000	2490	55
	P	18.0	1.0	0.1

8.7 Appendix G: Supplementary data for pH Vs L/S ratio in column leaching experiment for Akatiti tailings.

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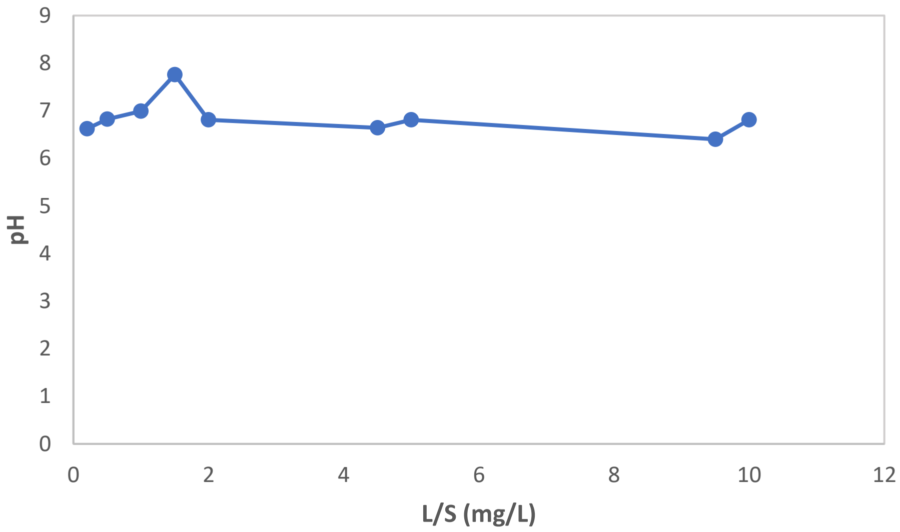


Figure 3-G Supplementary material for pH vs L/S ratio at neutral pH for Akatiti tailings column leaching test.

9.0 APPENDICES: Supplementary Information for Chapter 5

ENERGY EFFICIENT ROASTING AND REMEDIATION OF COPPER MINE TAILINGS VIA SMOULDERING

9.1 APPENDIX I: Temperature profiles for Akatiti and Uchi tailings

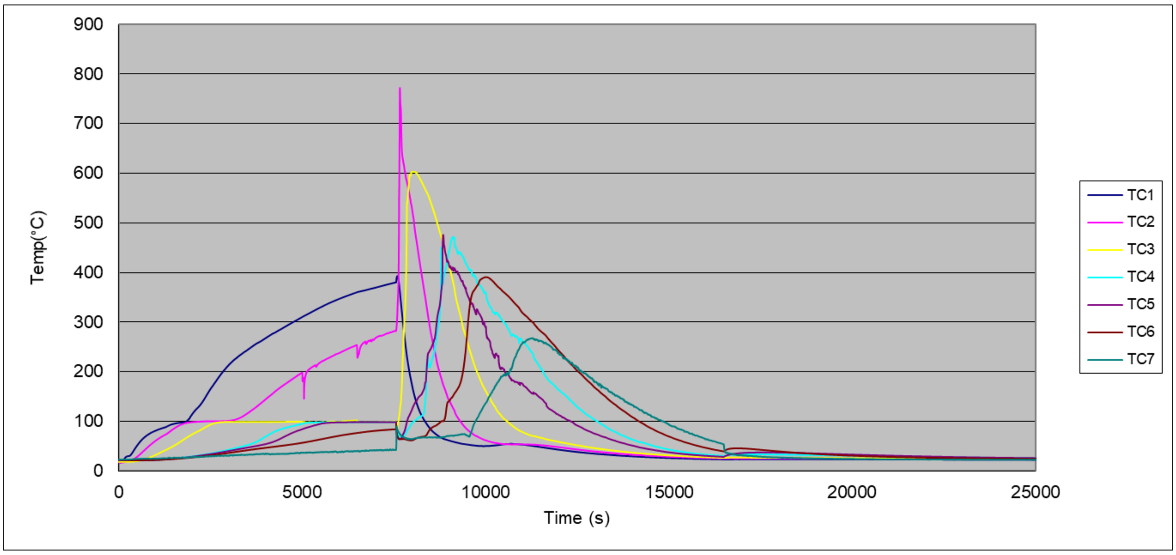


Figure 5-I: Temperature profiles for Akatiti tailings using vegetable oil as surrogate fuel for the smouldering treatment process.

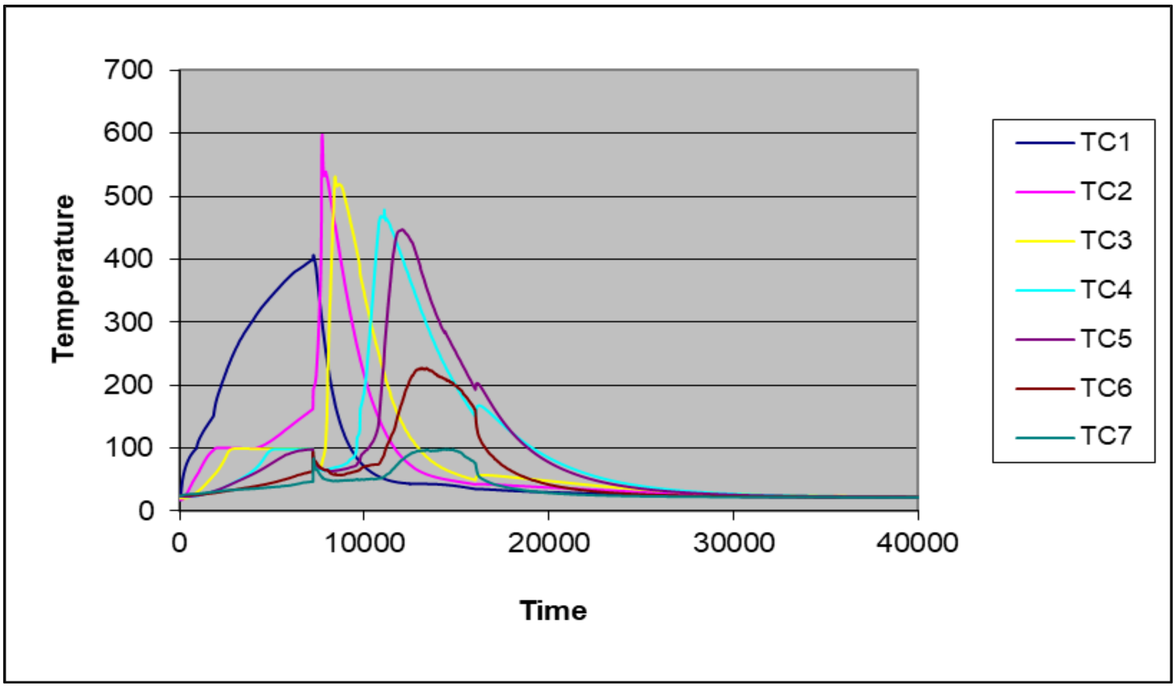


Figure 6-I: Temperature profiles for Uchi tailings using vegetable oil only as surrogate fuel.

Table 5.3 Mass loss after roasting Akatiti and Uchi tailings at 600 °C and 1000 °C (g/g dry tailings) respectively.

Sample ID	Container (g)	+ Tails (g)	+ 600 °C (g)	Tails (g)	Roasted tails (g)	Mass loss (g / g tails)	Mass loss (g / g dry tails)	Average mass loss (g/g dry tails)	Average mass by percentage (%)
A1	30.004	31.992	31.970	1.988	1.9658	0.011	0.011	0.012	1.2
A2	46.944	50.023	49.980	3.079	3.036	0.014	0.014		
A3	50.144	53.867	53.829	3.723	3.6847	0.010	0.010		
U1	50.158	51.762	51.736	1.604	1.5783	0.016	0.016	0.016	1.6
U2	47.055	48.518	48.490	1.463	1.4354	0.019	0.019		
U3	66.585	70.379	70.328	3.795	3.7432	0.014	0.014		
	Container (g)	**+ tails (g)**	**+ 1000 °C (g)**	**Tails (g)**	**Roasted tails (g)**	**Mass loss (g / g tails)**	**Mass loss (g / g dry tails)**	**Average mass loss (g/g dry tails)**	**Average mass by percentage (%)**
A1	30.012	33.144	33.027	3.132	3.015	0.037	0.038	0.038	4.0
A2	46.954	49.799	49.692	2.845	2.738	0.038	0.038		
A3	50.154	54.741	54.569	4.587	4.415	0.037	0.038		
U1	50.160	52.725	52.439	2.565	2.279	0.112	0.112	0.110	11
U2	47.054	49.183	48.954	2.129	1.900	0.107	0.108		
U3	66.587	67.864	67.725	1.277	1.137	0.109	0.110		

Key: Sample IDs in Table 5.2 with A represents Akatiti tailings and U represents Uchi tailings.

9.2 APPENDIX J: pH dependence leaching graphs for aluminium, nickel, sulfur and zinc.

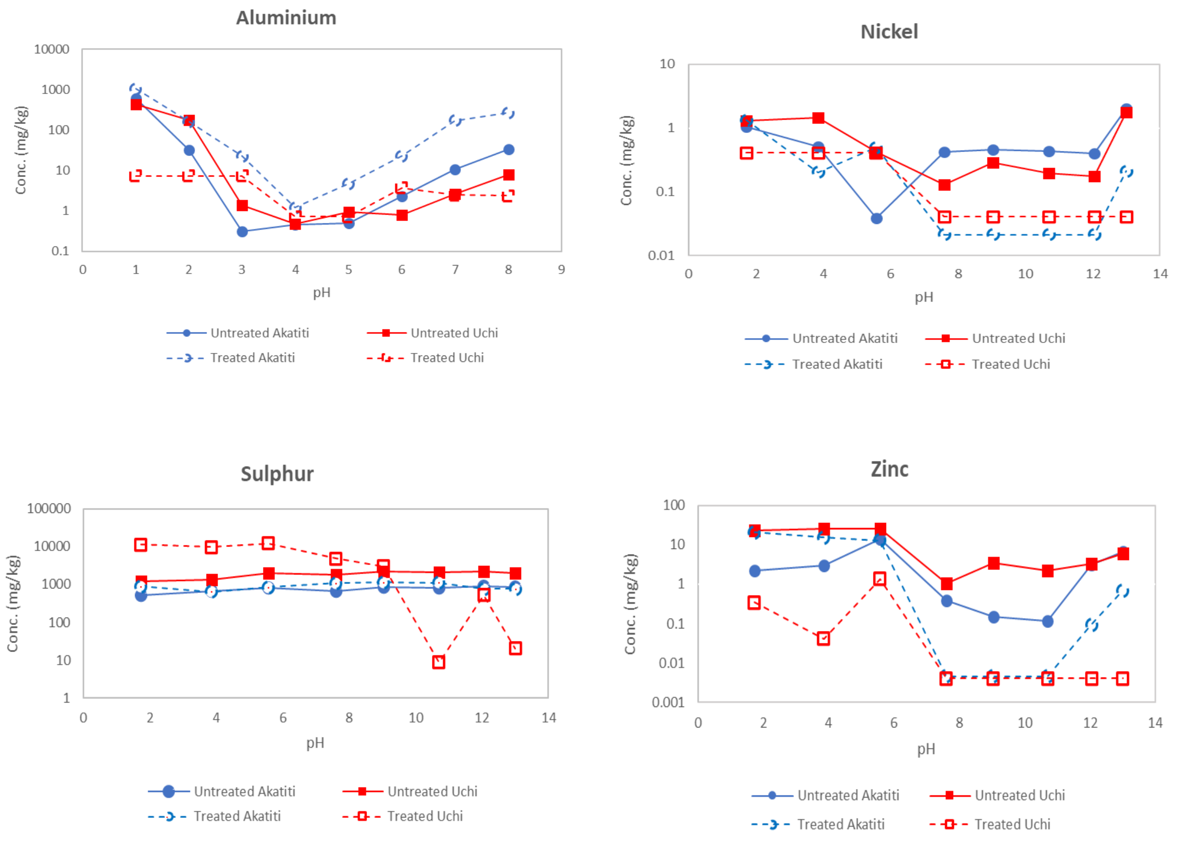
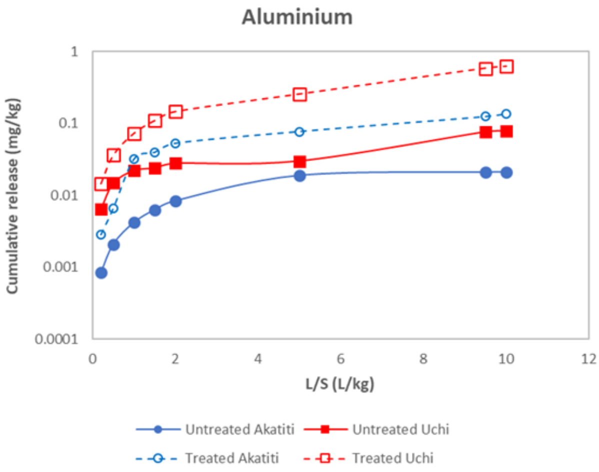
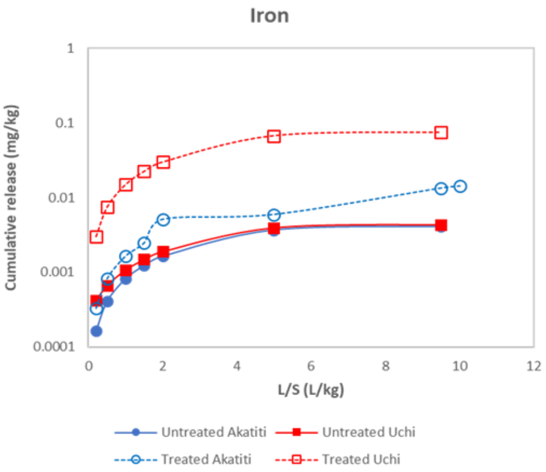
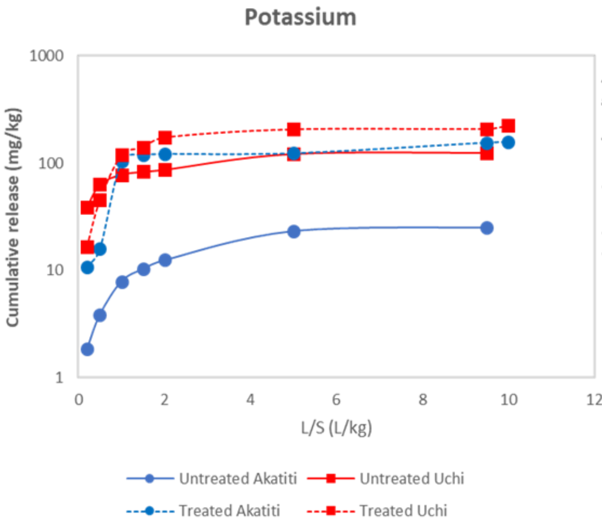


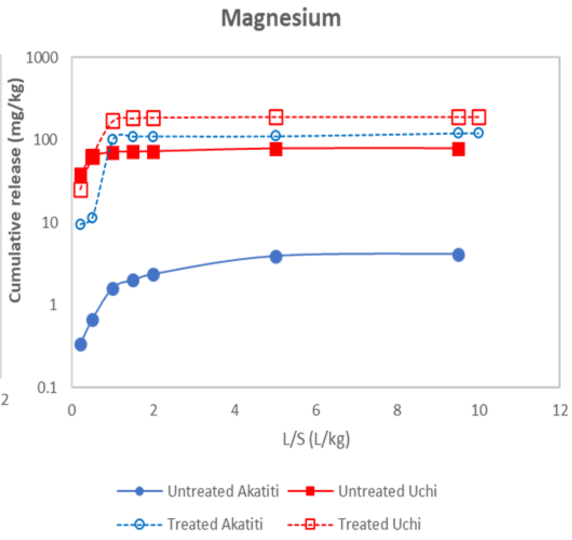
Figure 7-J: pH leaching graphs for aluminium, nickel, sulfur and zinc results in the untreated and treated tailings of Akatiti and Uchi tailings. The concentration of the available content in the leachate during leaching are presented in mg of element per kg dry tailings.

9.3 APPENDIX K: Column leaching graphs for Al, Fe, K, Mg, Na, Ni, P, Zn a in the untreated and treated Akatiti and Uchi tailings.









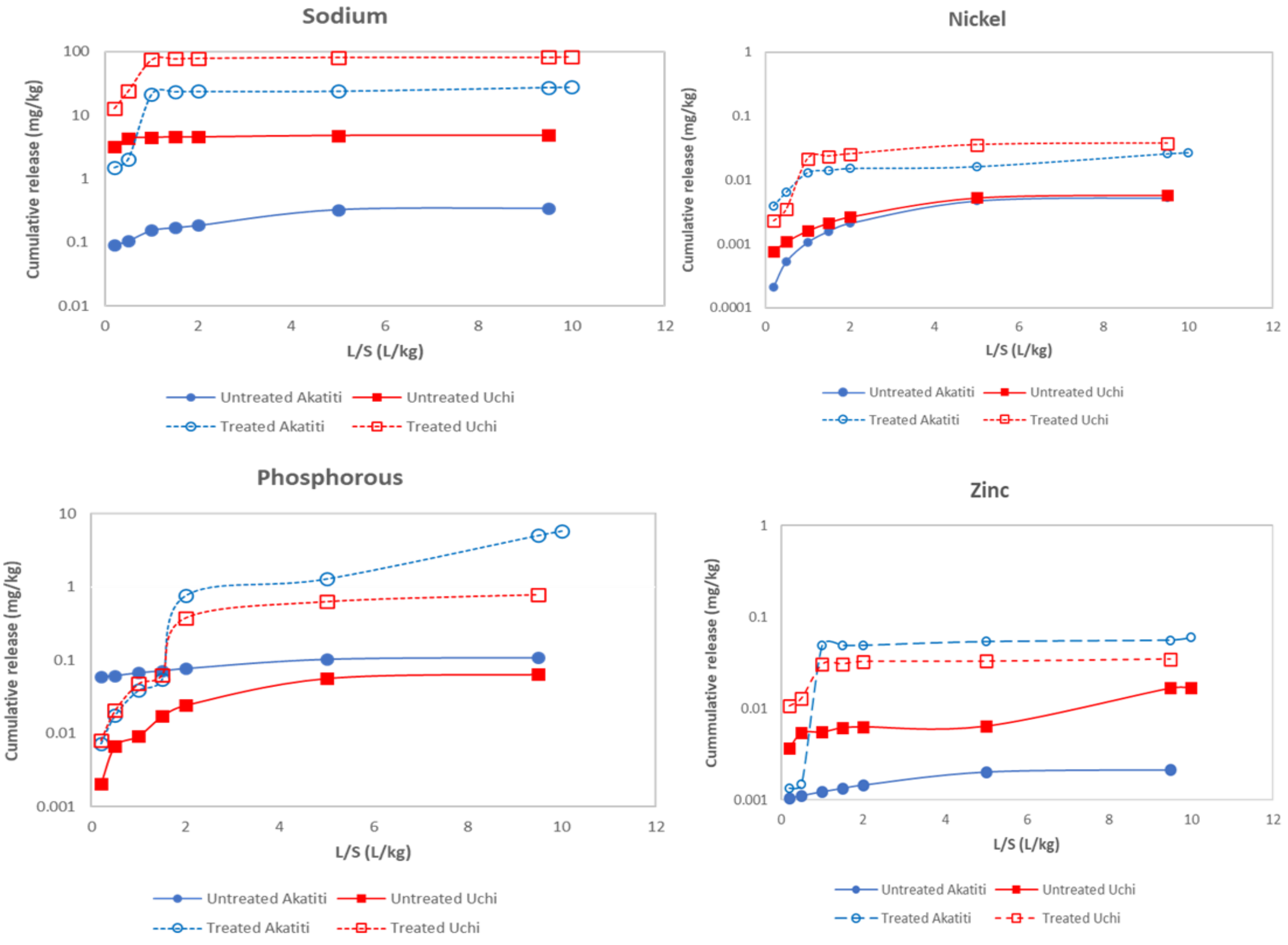


Figure 8-K: Column percolation results for Al, Fe, K, Mg, Na, Ni, P and Zn in the untreated and treated tailings of Akatiti and Uchi tailings. The PTEs are presented in mg of element per kg dry tailings.

9.4 APPENDIX L: Extraction efficiency of phosphorous and sulfur for the untreated, treated, and roasted tailings at 600 °C and 1000 °C for Akatiti and Uchi tailings.

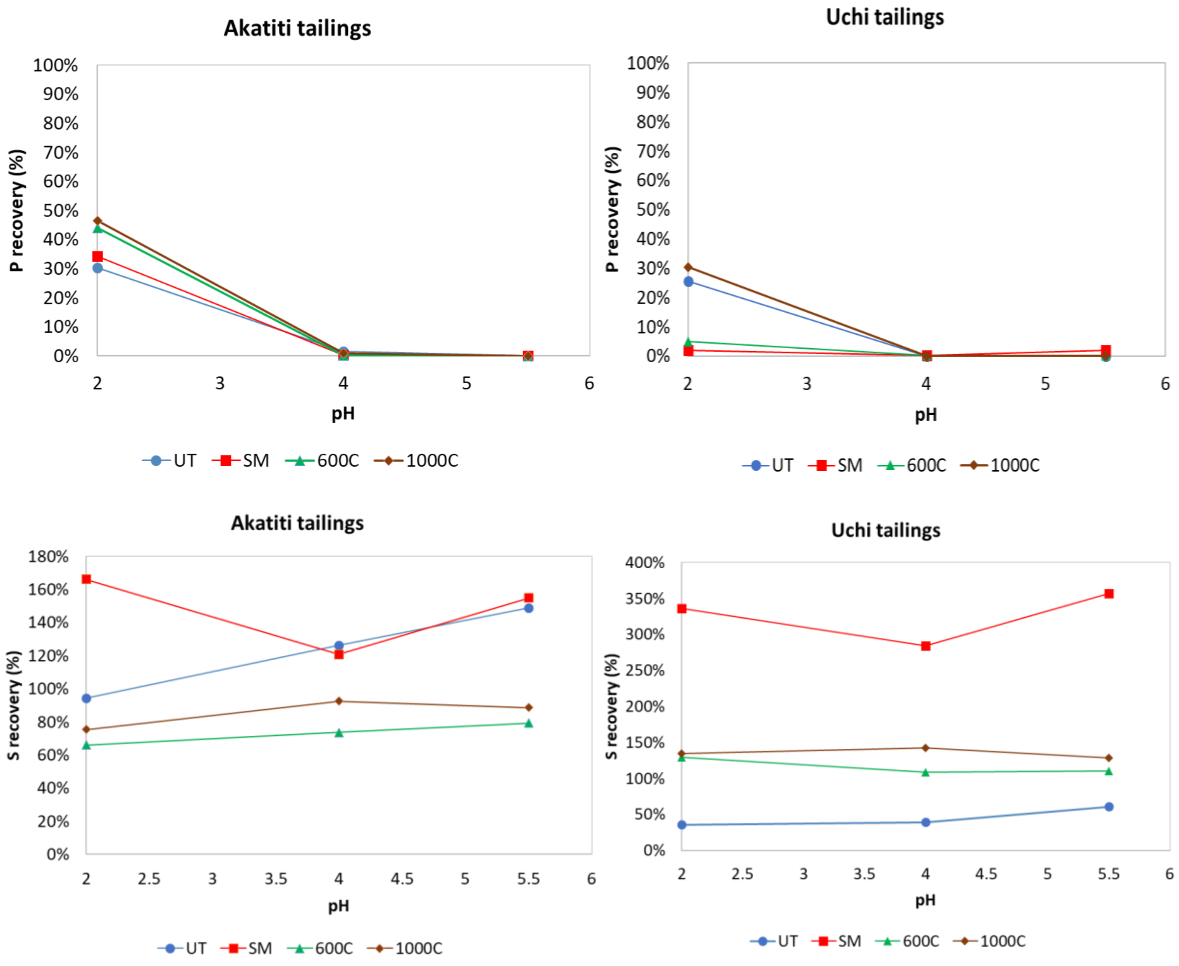


Figure 9-L. Recovery of phosphorous and sulfur using a pH dependence leaching test method at targeted pH values of 2,4 and 5 for the untreated, smouldered, and roasted temperatures.

10.0 Appendix: Supplementary Information for Chapter 6

10.1 APPENDIX M: Extraction efficiencies of copper using nitric acid at pH targets 2,4 and 5.

Table 6.3. Extraction efficiencies of copper for Akatiti, Kitwe and Uchi tailings in mg/kg-dry from the pH dependence test, Method 1313 for 24 hrs washing period.

Site	**Copper pseudo-total content**	**pH**	**Akatiti tailings**	**Kitwe tailings**	**Uchi tailings**	**Extraction efficiency, Cu (Akatiti)**	**Extraction efficiency, Cu (Kitwe)**	**Extraction efficiency, Cu (Uchi)**
Akatiti	8500	2	7079	3021	2497	83%	67%	40%
Kitwe	4480	4	6481	3248	2640	76%	73%	43%
Uchi	6200	5	38	3000	50	0.4%	67%	0.8%

10.2 APPENDIX N: Extraction efficiency of copper using 0.5M hydrochloric acid as leaching solution.

Table 6.4 Extraction efficiencies of copper for Akatiti, Kitwe and Uchi tailings using 0.5 M HCL for 24 hrs washing period.

Site	Copper pseudo-total content	Extracted copper with 0.5 M, HCl	Extraction efficiency (%)
Akatiti tailings	8500	8000	94
Kitwe tailings	*4480	*5078	*113
Uchi tailings	6200	5077	82

NB: *More extracted copper in Kitwe tailings may be caused by the higher dissolution of the copper oxides that maybe present in the tailings. The experiment may need to be repeated from various locations of the tailings site to confirm this extraction efficiency value.