Investigation of the effect of microorganisms and their metabolites on the mobility of metals in a gold tailing dump in South Africa

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DECLARATION

I Munyai Hlayisani Ashley hereby declare that this is a true reflection of my own work and has not been submitted for any degree or examination in any other University.

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PREFACE

Introduction

This Dissertation was submitted in article format as granted by the academic regulations of the North-West University (NWU). This entails that results and discussions, as well as the experimental chapter were not included in the thesis as such information was presented in the articles (Chapter3, Chapter 4 and 5). The chapters included in this thesis are as follows: Chapter 1, which presents the background, problem statement, aim and objectives, and a literature review (Chapter 2), conclusion and recommendations (Chapter 6). The journal articles (Chapters 3 and 4) were published by International Journal of Science and Research while chapter 5 will be sent for review. The numbering of figures and tables are not in line with that of the thesis as the articles were published before the writing of the thesis.

The reasons behind choosing the article format.

The requirement for the submission of MSc thesis at NWU is for a candidate to publish more than one paper from theMSc.

Authors of the articles (chapter 3-5) are as follows:

Chapter 3

Ashley H. Munyai, Elvis Fosso-Kankeu, FransWaanders

Biological influence on the mobility of metals from mine tailings dump located in Krugersdorp area.

Faculty of Chemical engineering and mineral, Northwest university, Potchefstroom campus, Private Bag X6001, Potchefstroom, South Africa

Chapter 4 (Article 2)

Ashley H. Munyai, Elvis Fosso-Kankeu, FransWaanders

Leaching of metals from mine tailings using organic acids: Batch leaching experiment

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Authors contributions:

The laboratory work and writing of an article were done by the candidate Ashley H Munyai, conceptual ideas and research planning were conducted by Prof Elvis Fosso-Kankeu (supervisor) and Prof FransWaanders (co-supervisor). That was vital to the writing of an article and also the field work. Prof Waanders also assisted in collection of samples (fieldwork).

Chapter 5 (Article 3)

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Column leaching of tailings dumps from gold mine in South Africa and implication of organic matters.

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Current status of the article

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Consent by co-authors

The following co-authors: E FossoKankeu and F.B Waanders have given their permission that the candidate H.A Munyai may submit the MSc Dissertation in an article format

ACADEMIC OUTPUTS

PUBLICATIONS

Ashley H. Munyai, Elvis Fosso-Kankeu, Frans Waanders. 2015. Biological Influence on the Mobility of Metals from Mine Tailings Dump Located in Krugersdorp Area. International Journal of Science and Research (IJSR). 5 (4), 1396-1403.

Ashley H. Munyai, Elvis Fosso-Kankeu, Frans Waanders. 2016. Mobility of Metals from Mine Tailings using Different Types of Organic Acids: Batch Leaching Experiment. International Journal of Science and Research (IJSR). 5 (11), 520-527.

Ashley H. Munyai, Elvis Fosso-Kankeu, Frans Waanders. Column leaching of tailings dumps from gold mine in South Africa and implication of organic matters. Submitted.

School of Chemical and Minerals Engineering, Faculty of Engineering, North-West University, Potchefstroom – South Africa

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Elvis Fosso-Kankeu, Frans Waanders, Ashley H. Munyai. Susceptibility of metals release from tailings dumps located in the Krugersdorp area. Proceeding of 7th International Conference on Latest Trends in Engineering & Technology (ICLTET'2015), Irene, Pretoria, South Africa, pp. 64 – 69

Ashley H. Munyai, Elvis Fosso-Kankeu, Frans Waanders. Effects of organic acids on metals released from mine tailings. International Conference on Advances in Science, Engineering, Technology and Natural Resources (ICASETNR-16) Nov. 24-25, 2016 Parys, South Africa

OTHER PUBLICATIONS RELATED TO THIS WORK

Fosso-Kankeu, E., Manyatshe, A., Munyai, A., Waanders, F. 2016. AMD formation and dispersion of inorganic pollutants along the main stream in a mining area. Proceedings IMWA 2016, Freiberg/Germany Drebenstedt, Carsten, Paul, Michael (eds.) Mining Meets Water – Conflicts and Solutions, pp. 391 – 397.

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Abstract

This study investigates the mobility of heavy metals and light metals in abandoned mine tailings dumps from the Krugersdorp. Most areas in South Africa which have mines are suffering from waste contamination. Tailings dumps deposited in the environment by mining companies contain residual heavy metals which are likely to be released and contaminate the environment. In South Africa tailings from the gold mines are of great concern, as such mines are regarded as the largest single source of pollution. Mine tailings are of great danger when not rehabilitated, as this facilitates erosion and washing away during rainfall. Oxygenated rainwater is able to combine with mine tailings and the pyrite minerals released to form acid mine drainage (AMD). There is a need to implement biological methods which are environmentally friendly and inexpensive, in order to solve the problems posed by mine tailings. Tailings samples from abandoned mine tailings dumps in the Krugersdorp mining area were considered, as human health seems to be of serious concern there. The samples were taken using an auger drill. From the top to the bottom of tailings dumps 14 samples were taken.

The chemical and mineralogical structure was analysed withX-Ray fluorescence (XRF) and X-Ray diffraction (XRD), respectively. The heavy metals were further analysed by inductively coupled plasma-optical emission spectrometry (ICP-OES). The results of the XRD have illustrated that quartz was the most abundant mineral in the tailings. Other minerals found were iron catena-silicate, ferrosilite, pyrophylite, hautrurite, andulusite, brown millerite and calcium iron (III) oxide, dialuminium silicate oxide, kyanite, dicalcium silicate and sillimanite. The XRF results showed that major elements were mostly in the form of SiO_2, Fe_2O_3 and Al_2O_3. Sequential leaching methods were employed to evaluate the availability of metals in the tailings and assess the potential risk of pollution. It was found that metals in the most labile fractions were more likely to be released than those which were in the residual fractions. FTIR analysis was performed to determine the functional groups likely to bind metals and prevent their mobility. The DNA sequencing outcome showed that heterotrophic microorganisms were represented by*Bacillus* sp and *Pseudomonas*sp and autotrophic microorganisms were represented by*Leptospirillumsp and Sulfobacillus sp.* Batch leaching tests were implemented in order to determine the impact of organic acids, which are released by microorganisms, on the mobility of metals. The findings showed that at high temperatures and concentrations of organic acids the mobility of metals increased. The column leaching method was used in order to simulate the exact field conditions, as the freshly collected samples from the field were used without crushing and drying. Compost was used to assess the role of organic material with a view of revegetating metal-contaminated areas. It was established that the addition of compost affects the metal mobility and the oxidation of mineral sulphides. High concentrations of sulphate was found, the mobility was also restricted by the addition of compost. Metal speciation results determined by the PHREEQC model have shown the presence of free metal ions in the leachate which are more mobile compared to metal occurring in a complex form, which makes distribution of metals on the surface more likely to cause contamination.

Keywords: metal mobility, heavy metals, AMD, Tailings, organic amendment, compost, microorganisms, metal speciation, dump, sample, FTIR.

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LIST OF ABBREVIATION

ORP	Oxidation – reduction potential
ICP-OES	Inductively coupled plasma spectroscopy
XRD	X- ray diffraction spectroscopy
XRF	X-ray Fluorescence spectroscopy
FTIR	Fourier transformation infrared
NRF	National Research Foundation
EC	Electrical Conductivity
NWU	North – West University
AMD	Acid mine drainage
OC	Organic carbon

Fe	Iron
Ni	Nickel
Cu	Copper
NP	Neutralization Potential
AP	Acid Potential
H	Hour
O_2	Oxygen
CO2	Carbon dioxide
C	Carbon
N	Nitrogen

CHAPTER 1

Background, motivation and objectives

1.1 Introduction

This chapter presents an overview of the aim and objectives of determination of the effect of microorganisms and their metabolites on the mobility of metals in gold mine tailings dumps. In 1.2 backgrounds information, as well as the significance for this study is covered, while the aims and objectives are presented in 1.3.

1.2 Background and motivation

Mine tailings are a major cause of heavy metal pollution in the soils, surface and ground waters (Seh-Bardan *et a*l, 2009). Mines are very important to the world economy, which is the reason why mining activities cannot be avoided. Mining and metallurgical activities cause a massive amount of mine tailings, which has become a major problem. In South Africa, and most parts of the world, there are abandoned mine tailings which are left without any treatment or not properly managed. Furthermore, some of the mining companies which have ceased activities are also abandoned. South Africa has many abandoned mine tailings dams, some of which were abandoned many years ago. These abandoned mine tailings dams cause many problems as they encroach water streams and other neighbouring areas, because they were not rehabilitated or covered. Mobilization of the heavy metals from mining areas to the neighbouring environment could have an impact on contamination of soil, pollution of water and causing other serious environmental issues (Nguyen *et al.*, 2015). In South Africa, most tailings dams and unrehabilitated footprints of re-mined tailings dams are unfenced and even used for recreation (e.g. by quad-bikers), as informal playgrounds by children, and for livestock grazing (Liefferink, 2007). The unfenced and unrehabilitated mine tailings cause the soil to be easily eroded during rainy seasons and windy times. In addition to increasing erosion and dust emissions, the increased ingestion of particles by young children is known to place this population group at particularly high risk of metal toxicity (Liefferink, 2011). The mine tailings dumps can cause air pollution when they are not covered (Wright *et al.*, 2014).The pollution can be seen in affected neighbourhood like Davidsonville, Kagiso and Krugersdorp, in the Witwatersrand area (the Gauteng province), who live alongside these gold mine dumps and tailings dams (Wright *et al.*, 2014).The unmanaged mine tailings dams canweather and mobilize the metals from minerals such as pyrites and other sulphides resulting in acid mine drainage (AMD). The mine tailings dumps in abandoned mines in Krugersdorp are a great danger as they have eroded due to rain and washing away to the bottom of the dump. The first acid mine drainage has been found in that area.

Due to metals hazardous to the environment, most studies have used different methods in order to assess the mobility of metals released from mine soil (Fan et al., 2016, Arwidsson and Allard, 2010 and Misra *et al.*, 2009). Specifically mobility of metals was predicted with the use of methods such as sequential leaching, batch leaching and column leaching. Sequential leaching is carried out in order to leach out heavy metals from soil fractions (Pueyo *et al* 2003). The batch and column leaching are able to simulate the leaching of mine soil to predict the release of the metals providing the idea of how dangerous mine waste is to the environment (Kundu *et al* 2014). However the column leaching predicts the prevailing environmental situation than the laboratory batch leaching (Lackovic 2007), as fresh sample from the field is used than at batch leaching where dried and crushed sample is used. Concerning that it means column leaching can predicts the potential mobility and bioavailability of metals.

The importance of mining compels people around the world to continue the mining and metallurgical activities, resulting in the accumulation of mine tailings dumps affecting human beings and organisms that depend on the contaminated environment. Removal of toxic elements in mine tailings is necessary (Seh-Bardan *et al.*, 2012; Wang and Mulligan 2009). In that regard many studies have conducted bioleaching processes in order to solve the contamination problem (Ahmadi *et al.*, 2015; Amiri *et al.*, 2012; Mishra et al., 2005; Liu et al., 2008; Serbadan *et al.*, 2012). There is a need to carry out an investigation that will help the stakeholders to predict mobility of metals in tailings dumps and the potential of beneficiation through biological and eco-friendly methods. Finding an effective way of extracting and recovering those metals, will increase the economy of the country and mitigate the negative impact on the environment.

Figure 1: The mine tailings dumbs in the Krugersdorp mining area

1.3 Problem statement

Tailings dumps placed in the environment by mining companies contain residual heavy metals which are likely to be released and contaminate the environment. The mobility of these metals from tailings dumps is site specific as the mineralogical composition of the tailings dumps, as well as the weather of the particular area, are the determining factors. It is therefore important to carry out an investigation to predict the mobility and the bioavailability of metals from tailings dumps as such studies have not yet been done in the area of investigation. Furthermore, another consideration could be the beneficiation of some abundant metals, using suitable techniques.

1.4 Aims and objectives

1.4.1 Aim

To determine the mobility and bioavailability of metals in tailings dumps and investigate the potential of biological methods for their extraction.

1.4.2 Objectives

(i) To determine the concentrations of residual metals in tailings dumps in Krugersdorp area of South Africa
(ii) To investigate the effectiveness of organic amendment for the management of tailings dumps
(iii) To determine the potential of microorganisms and their metabolites for the removal of metals
(iv) To predict the mobility of metals released from tailings dumps located in the Krugersdorp area of South Africa.

1.5 Research questions

The research questions were formulated in order to provide an answer to the purpose of the study and are as follows:

- Which residual metals are present in mine tailings dumps of interest?
- What is the influence of the organic acids to the mobility of metals during different environmental conditions?
- Which microorganisms are found in mine tailings?
- What is the effectiveness of organic amendments with regard to the immobilization of metals in the tailings dumps?

1.6 Dissertation structure

In order to accomplish the purpose of this study, the structure was constructed. This dissertation is divided into six chapters including this chapter (chapter 1) and an Appendix.

Chapter 1: **introduction**

A brief background of the mine tailings contamination, motivation and significance of the study and the research questions and also specific objectives of the study are covered.

Chapter 2: **Literature Review**

The literature study presents an overview of what others have done which is relevant to the current study. In that regard environmental pollution by metals from mine tailings together with it management has been discussed.

Chapter 3 to chapter 5 are given in article format as it was already stated in the preface.

The three chapters (3 to 5) are as follows:

Chapter 3: Biological influence on the mobility of metals from mine tailings dump located in Krugersdorp area addresses the susceptible release of metals from tailing dump.

Chapter 4: Mobility of metals from mine tailings using different types of organic acids: Batch leaching experiment, was conducted in order to satisfy objective (i) and (ii).

Chapter 5: Column leaching of tailings dumps from gold mine in South Africa and implication of organic matters was conducted to address the effectiveness of organic amendment of tailings dump.

Chapter 6:Conclusion and recommendations

It summarizes the results and discussion and it also suggest what could be done in future for the follow up of this study.

In the end of this thesis is the appendix A, which is showing the pictures for mine tailings sampling sites, from the top, middle and bottom of the dump.

References

1. Ahmadi A, Khezri M, Abdollahzadeh A.A, Askari M, (2015. Bioleaching of copper, nickel and cobalt from the low grade sulfidic tailings of Golgohar Iron Mine, Iran. *Hydrometallurgy*.(154) 1–8.

2. Arwidsson Z. and Allard B. Remediation of metal-contaminated soil by organic metabolites from fungi II—metal redistribution. *Water Air Soil Pollut*. 207: 5–18 (2010).

3. Amiria F, Mousavic S.M, Yaghmaeia S., Barati. M, (2012). Bioleaching kinetics of a spent refinery catalyst using Aspergillusniger at optimal conditions. *Biochemical Engineering Journal*. 67, 208– 217.

4. Kundu S, Rathore A.S, Pushp A &Chundawat V.S, 2014. Batch Investigations on Elemental Dissolution from Copper Mine Tailings Pond, Khetri, India: Evaluation of the Environmental. Contamination Potential International Conference on Chemical, Civil and Environmental Engineering.18-19.

5. Lackovic A.J.A, Nikolaidis N.P, Chheda P, Carley R.J and Elsie P, 2007. Evaluation of bath leaching procedures for estimating metal mobility in glaciated soil. *Ground water & Remediation*. 17, 231-240.

6. Liefferink, 2011.Assessing the past and the present role of the National Nuclear Regulator as a public protector against potential health injuries: *The West and Far West Rand as case study*

7. Nguyen V.K, Lee M.H, Park H.J, Lee J, 2008. Bioleaching of arsenic and heavy metals from mine tailings by pure and mixed cultures of Acidithiobacillus spp. *Engineering Chemistry*. 21,451–458.

8. Omar R. Salinas Villafane, Toshifumi Igarashi, Mitsuru Kurosawa & Toshio Takase, 2012. Comparison of potentially toxic metals leaching from weathered rocks at a closed mine site between laboratory columns and field observation. *Applied Geochemistry*.

9. Seh-Bardan B.J, Othman R, Wahid SA, Husin A, and Sadegh-Zadeh F, (2012). Bioleaching of Heavy Metals from Mine Tailings by Aspergillus fumigatus. *Bioremediation Journal*. 16, 57–65.

10. Wang J, Huang Q, Li T, Xin B, Chen S, Guo X, Liu C, Li Y, (2015). Bioleaching mechanism of Zn, Pb, In, Ag, Cd and As from Pb/Zn smelting slag by autotrophic bacteria. Journal of *Environmental Management*. 159, 11-17.

11. Wright CY, Matooane M, Oosthuizen M.A and Phala N, Risk perceptions of dust and its impacts among communities living in a mining area of the Witwatersrand, South Africa. *Clean Air Journal. Vol 24, No.1*.

CHAPTER2

Literature Review

2.1 Introduction

General information from the literature survey related to this study is provided in this chapter. The following information is presented: The issue of mine tailings dumps is a concern to the environment, as it produces toxic elements **(2.2.1).** Accumulation of tailings from tailings dump sat South African mines, and the risk associated with residual mine tailings. **(2.2.2)**. This chapter also presents the problem of acid mine drainage **(2.3)**and gives details about the microorganisms found in mine tailings which can be used to release metals. **2.4** It also surveys information about the management of mine tailings by using organic amendment and by using microorganisms. **2.5**and**2.6** provide details about the microorganisms in the leaching of metals. **2.7** explain the use of organic acids in mobilizing metals. **2.8**. It provides the conclusion of the literature survey.

2.2 Mine tailings and acid mine drainage

2.2.1 Mine tailings disposal

Mine tailings are wastes product of mining, which consist of fine grained sand and also contain various minerals (Mine tailings can be referred to as mine soil (Stoltz and Greger, 2006). Environmental contamination by heavy metals is a big concern nowadays in mining industry. Mine activities are not environmentally friendly because of huge amounts of wastes such as tailings and slag which are deposited in areas (Misra, 2009). Mine tailings are the major source of pollution in the soil and water due to the fact that they release toxic heavy metals (Doumett et al., 2008; Lim et al., 2009; Feasby and Temblay1995). Heavy metals are not a subject to degradation process that is the reason concentrations of such metals remain for prolonged period, although bioavailability of these metals can greatly change, depending on their interactions with the various soil constituents (Doumett et al., 2008). Mine tailings are a huge source of pollution by arsenic (As) and heavy metals in soils and water from the ground (Wang and Mulligan

2009 as cited by Seh-Bardan et al, 2009). Most of these mine tailings are left unmanaged in most mines (Zhong-bing et al., 2012), especially in the situation where by these mines have ceased the activities. The unmanaged tailings results in the mobilization of heavy metals to the neighbouring areas thus, cause environmental pollutions (Liu et al., 2008). In South Africa, waste from gold mining was estimated to contribute more to pollution than any other source (Oelofse 2007, DWAF, 2001). Examples of gold mine tailings causing pollution in the neighbouring areas have been mostly from the areas around the Gauteng province, for example the Witwatersrand mining basin. In this basin gold and uranium are more abundant than the other minerals, which make it the largest basin of the two minerals in the whole world (Liefferink, 2014). Mine tailings contain huge amounts of sulphide minerals, such as pyrites which are estimated to be between 10 and 30 kg/ton and thus is likely to cause acid mine drainage (AMD) (Rosner and Van Schalkwyk, 2000).

2.2.2 Generation of Acid mine drainage

AMD characteristics are generated when acidity is very high (low pH), when the sulphate and heavy metals concentrations are high. AMD is generated when iron sulphide is exposed to water and air. The exposure of such sulphide to water and oxygen convert its material into sulphuric acid and iron composite by oxidation (Davies, 2012). Such oxidation results in AMD, which is able to deteriorate streams because of its low pH and which results in mobilization of metals (Jia*et al.*, 2014). The oxygenation process happens when oxygenated rainwater combines with mine tailings (Grover *et al.*, 2016;Stumm and Morgan, 1996).AMD generation can be enhanced by bacteria occurring naturally, which is able to break the mineral sulphide (Akcil and Koldas, 2006). In South African gold and coal mines, iron pyrites (FeS_2) are present as sulphide minerals. Here are four basic steps in the oxidation of pyrite (Grover *et al.*, 2015).

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \qquad (1)$$

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow F^{3+} + 1/2H_20 \qquad (2)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (3)$$

Ferric iron can be released from the solution at pH greater than 3 by hydrolysis and that can be depicted by the following reaction:

$Fe^{3+} + 3H_2O \rightarrow Fe\ (OH)_3 + 3H^+$ (4)

The factors needed for the AMD generation are sulphides from mine wastes, oxygen and water exhibited in equation 1 and 2, the other components which can cause the AMD are temperature, pH the activity of a bacteria and ferric ion (Fe^{3+}) shown in equation 3 (Kuyuk, 2002).

The AMD have a negative impact on the ecosystem such as contamination of water, disruption of plants and killing of animals which depends on streams water (Wali et al., 2014). There are several methods which were taken in order to mitigate AMD that include neutralization by the use of limestone, hydrated limestone and also the ammonia (Campaner et al., 2014)

2.2.3 History of Acid mine drainage in South Africa

AMD is of great concern in most areas worldwide. In South Africa, the deleterious effect of AMD is found in the mining area sites at West Rand in Gauteng Province, where acid water from the mine begun to pour out from the underground at the abounded mine sites in August 2002 (Oelofse, 2008). In 2005, the decantation was about 15 mega litres per day (ML/d).The AMD flowed towards the Cradle of Humankind World Heritage site and the game Reserve it has contact with Natural water" (Oelofse *et al.*, 2007).Other areas in the Gauteng province which also have an AMD problem are areas such as the Witwatersrand and Krugersdorp. However, the Witwatersrand is the great area of concern, as such acidic water is apparently destructing streams in this area (Naicker et al., 2003).However, the Witwatersrand is the great area of concern. In 2002, the AMD also welled up and began pouring out from underground on the vicinity of Krugersdorp area, and from that year until now, about 15 million litres of AMD is been overflowing a day, and AMD have been spilling out (DuToit 2011).

2.3 Microorganisms in bioleaching

Mobilization of metals by microorganisms can be presented by means of processes such as chelation, biological substances, methylation and also siderophores (Gadd, 2004). The microorganisms that take part in bioleaching process are: autotrophic bacteria which are able to absorb carbon from carbon dioxide and heterotrophic bacteria and fungi, which are able to absorb organic carbon (Khoshkoo, 2014). These microorganisms find the energy by cracking down ores into its elemental supplements (Vukovic et al, 2014). The mostly used autotrophic bacteria in bioleaching processes are *Chemolithotrophic* bacteria of genus *Acidithiobacillus and Thiobacillus,* such as *T.ferroxidans* and *A.thiooxidans* and *Thiobacillusthioparus* (Liu *et al.*, 2007;Ngunyen *et al.*, 2014; Park *et al*; 2014). Heterotrophic bacteria include *Bacillus licheniformis* and *Bacillus polymyxa*, and examples of fungi species are *Aspergillum niger and Penicillium simplissimum.* Fungi species like*Penicilliumsimplissimum* and *Aspergillus niger* are also some of microorganisms which are used in the industry for recovery of metals from its ores, especially the non-sulphide in bioleaching processes (Lee *et al.*, 2011; Brandl and Faramarzi, 2006; Bosecker, 2007).

Most naturally occurring bacteria and fungi accomplish numerous physiologically important reactions that enable them to grow and reproduce (Bosecker, 1997). Basically the impact of bacteria and fungi on metalsare onfour mechanisms, namely: (i) acidolysis, (ii) complexolysis, (iii) redoxolysis, and (iv) alkylation (Bosecker, 1997;Brandl, 2001;Brandl and Farmarzi, 2006). Bacteria and Fungi are able to promote the mobility of metals by using the following processes: Formation of organic and inorganic acids, secretion of complexing agents, oxidation and reduction reactions (Bosecker, 1997). Organic acids are produced by heterotrophic microorganisms, whereas inorganic acids are produced by autotrophic organisms. The autotrophic microorganisms utilize atmospheric CO_2 from carbon and find energy for multiplication from the process of ferrous oxidation process which assembles acidic condition needed for metal extraction from the soil (Park *et al.*, 2014). Autotrophic bacteria are called Sulphur-oxidizing bacteria, as they are capable of oxidizing the sulphides minerals to sulphates and thus cause the metals to be released (Coto *et al.*, 2008Rawling, 1997). Those bacteria which are capable of oxidizing sulphur are frequently used in leaching of ores from sulphide (Coto *et al.*, 2008).However the non sulphidic ores like oxides, carbonates and silicates, which does not have energy source for microorganisms can be released by heterotrophic bacteria and fungi which get energy from organic carbon and also get its carbon for growth (Jain and Sharma, 2004). Bioleaching of oxides, carbonates and silicates ore and minerals are utilized for metal recovery from the mine wastes (Jain and Sharma, 2004).

2.4 THE MANAGEMENT OF MINE TAILINGS

2.4.1 Bioleaching

Bioleaching is generally described as a utilization of microorganisms to dissolute metals from their mineral source in order to remove metals from materials when water is passed through (Brandl and Faramarzi, 2006). This method is mostly used in industries .Dissolution of metals from mine ores or tailings is possible if high acidic medium is created (Mulligan *et al.*, 2004).The solubilization of metals from their ores produces concentrated solutions of metal such as copper, gold, uranium etc, which can be recovered by hydrometallurgical processes (Mishra*et al.*, 2005). Thedissolution of metals from mine wastes can be attained through various Acidophilic and chemoautotrophic bacteria like*Acidithiobacillusthiooxidans* and Acidic *Thiobacillusferrooxidans* which are autotrophic (Liu *et al.*, 2007; Liu *et al.*, 2008). Metal solubilisation from solid waste is obtained from the heterotrophic bacteria and fungi. Metal solubilisation are applied in order to extract and recover metals from solid wastes, ores and sediments from contaminated sites (Anjum*et al.*, 2012; Asghari*et al.*, 2013; Brandl, 2001; Watling, 2006). The bioleaching effectiveness is due to the chemical, physical and biological factors which are as follows: pH, Oxidation reduction potential (ORP) and bacterial strain (Zhong-bing*et al.*, 2011).

There are conventional methods, such as incineration and the use of chemicals which are used as the alternative to bioleaching for removal of metals from polluted soil (Praburamanet al., 2015).These conventional methods have been used for metal recovery, however they have some restriction like it being expensive, having low efficiency and long repair cycle (Zhong-bing*et al.*, 2011; Dong *et al.*, 2011).Compared to these conventional methods, bioleaching system are able to treat even low grade ores because of an added advantage like it being inexpensive, being a quick process, simple to manage and it being an environmental friendly process (Dong *et al.*, 2011).In that regard Brandl (2001); Nguyen and Lee (2015) have indicated that the bioleaching is an environmentally friendly in comparison with the chemical methods and not hazardous to the atmosphere (Brandl, 2001; Nguyen and Lee, 2015). This process is commercially used to process minerals such as copper, nickel, cobalt, zinc, lead and uranium (Vuković *et al.*, 2015; Dong *et al.*, 2011; Kim *et al.*, 2009**)**. The bioleaching is a favourable process because it depends on biological, chemical and physical factors (Zhong-bing *et al.*, 2011), like temperature, pH sulphur condition and bacterial contents (Bosecker, 1997).

2.4.2Organic amendment in tailings management.

Organic matter is mostly used in tailings rehabilitation (Li et al, 2013). Mine tailings which are the waste by-product from the mines have been revegetated by application of organic amendments like compost mixed with carbonate or limestone residuals (Brown *et al.*, 2007; Brown *et al.*, 2003, and DeVolder *et al.*, 2003). Organic amendments application to agricultural soil is more important to expect as it consists of nitrogen and phosphorus and it also able to better the structure of degraded soil (Shwab and Banks, 2007).

In the place where mining activities have ceased, tailings are likely to erode as it surface become dry due to climatic conditions and water table(Young *et al.*, 2015), but when the mines are active the ponded water tend to cover the tailing impoundments. The use of organic matter for amendment of soil or tailing can maintain the percolation of oxygen (O_2) in their biodegradation pathways (Cousins *et al.*, 2009; Markewitz *et al.*, 2004), as the influx of O_2 can have a potential to reduce acidification which can further decrease the mobility of metals (Cousins *et al.*, 2009).Even though application of organic amendment decrease bioavailability and the mobility of metals, if this organic amendment have weathered, mobility of metals can be enhanced (Mendez and Maier, 2008). It can also improve soil structure and aeration, reduces erosion, and increases infiltration (Mendez and Maier, 2008; Young *et al.*, 2015).

Different organic acid and inorganic wastes such as red gypsum, sugar foam, sewage sludge, biosolids, fly ashes, pig manure, marble wastes, etc., have been evaluated as amendments to improve some physical, chemical and biological factors of mine tailings and contaminated soils (Santos *et al.*, 2013; Forsberg *et al.*, 2008; Perez-Lopez *et al.*, 2007; Rodriguez-Jrda *et al.*, 2012; Zanuzzi *et al.*, Kuyuk, 2006). Sewage sludge has organic amendment which can be used as to revegetate the mine tailings and can also be used as a barrier which limits the influx of oxygen into the mine tailings (Neuschütz and Greger-Peppas *et al.*2000). Woodchips can manage the tailing environment by supplying the imbalance carbon which increases the activity of microorganisms as they are mainly comprised of carbohydrates (Li *et al.*, 2013; Mendez and Maier, 2008).That implies that such organic matters can be ably to mix with tailings and that will have an impact on covering for the oxygen not to diffuse to it (Li *et al.*, 2013). The decomposition and weathering of organic amendment can be prevented by the use of C to N which is ranging between 12:1 and 20:1, if organic amendments have high C:N ration thus will hinder the mobility of metals (Mendez and Maier, 2008;VanRensburg and Morgenthal 2004).

2.5 Release of metals by the use of autotrophic microorganisms

The releases of metals by autotrophic microorganisms are due to the proton-induced mineral dissolution with species such as *Acidothiobacillus ferroxidans, A.thiooxidans, Leptospilliium ferroxidans, Liferriphilum* (Guo *et al.*, 2013). Two mechanisms are involved in leaching with autotrophic microorganisms. The first mechanism is the direct mechanism which requires the interaction of bacteria with the surface of mineral and the sulphate oxidation by using catalytic reactions (Bosecker, 1997). In this case the bacterial cells will have to be bound to the surface of the mineral as close interaction is required

(Mishra *et al.*, 2005). In that regard Watling (2006) has shown that interaction between the bacterial cells and the mineral surface is conducted using biological methods without the use of ferrous or ferric ions. The second mechanism is the indirect mechanism whereby the oxidation of metals is accomplished by the ferric (III) ion which can oxidize metals to ferrous ion by using autotrophic microorganisms (Mishra*et al.*, 2005).

Bioleaching processes are basically on the activity of *T. ferrooxidans*, *L. ferrooxidans* and *T. thiooxidans* which oxidize the sulphide metals to sulphates (Bosecker, 1997.The oxidation and reduction for direct and indirect mechanisms can be outlined by their action steps. In that principle indirect and direct can be used to remove metals from sulphide by using a bacteria leaching (Bosecker, 1997). The traditional hypothesis that bacteria oxidize either through a direct / indirect mechanism takes placethrough biological or chemical reactions to interact bacteria and sulphide minerals (Mishra *et al.*, 2005). Tribotsch (2001), as cited by Lee and Pandey (2012), has coined the term “contact leaching” because it explains the interaction of bacteria with surface of mineral instead of by means of attack. The autotrophic organisms can be referred to as an acidophilic. These bacteria are able to oxidize sulphide metals into sulphate in the direct process, whereas for indirect process it produces$H_2SO_4$from oxidation or reduction of sulphur element (Liu et al 2007), and the direct and indirect mechanisms are explained by the pursuing equations:
The direct mechanism:

$MS + 2O_2 \rightarrow MSO_4$.. (1)

The indirect mechanism:

$SO + H_2O + 1.5O_2 \rightarrow H_2SO_4$.. (2)

H_2SO_4+materials-M → materials-2H + MSO_4....................... (3)

2.6. Mobilization of metals by heterotrophic microorganisms

Heterotrophic microorganisms like bacteria and fungi feed on organic matter for growth and energy and thus may be involved in leaching of metals (Bosecker, 1997). The interaction between these microorganisms and the surface of mineral is due to the carbon supplement they breakdown for energy supply (Jain and Sharma, 2004). Such microorganisms especially those which can work at neutral pH can be able to mobilize metals by complexing agents released (Brandl and Faramarzi, 2006). Heterotrophic microorganisms excrete organic acids like oxalic and citric acids, mostly used in bioleaching of non-sulphide ores and minerals (Coto *et al.*, 2008). Serh-Bardan *et al.* (2012) have established that these various organic acids are effectively released by fungi in the presence of heavy metals. Leaching of metals by heterotrophic is basically by means of indirect mechanisms together with a biological release of organic acids and other substances (Bayard *et al.*, 2006). In this regard Armiri *et al.* (2012) have established that the mostactive fungi in leaching of metals are species such as *Aspergillus or Penicillium species* with the ability to excrete large amounts of leaching agent such as organic acids. The heterotrophic microorganisms are used to treat silicate mineral and oxide in order to remove the metals by acid production, chelation of around the mineral and also by mineral oxidization (Lee and Pandey, 2011).

2.7 Mobilization of metals by complexing agents and organic acids

Various organic acids are produced by bacterial and fungal processes which cause, acidolysis and complexolysis formation (Brandl and Faramarzi, 2006). Complexation of metals by organic molecules is vital in the determination of metals speciation while acidolysis process is important in mobilizing metals from the environment (Gadd, 2004, Sayer *et al.*, 1999). Organic acids are able to bring ligands or chelating agents which chelate around heavy metals and promote their mobility (Burckhard *et al.*, 1995). Organic acids such as oxalic acids, malic and citric are reported to be working as a leaching agent in the process of leaching (Burckhard *et al.*, 1995). Organic acids are capable of providing anions and proton as complexing agents, which chelate around the metals (Gadd, 2004; Burgstaller and Schinner, 1993; Gadd, 1999; Gadd and Sayer, 2000). Citrate and oxalate anions can complex with a number of metals, for example copper and zinc, and highly mobile complexes may be resistant to biodegradation (Gadd, 2004; Gadd 2001). Almost all transition metals form good complexes with cyanide, which is able to solubilise highly in water and also show chemical stability (Brandl and Faramarzi, 2006; Chadwick and Sharpe, 1966).Studies whereby metals are solubilized by the formation of Cyanide complexes are limited, except in the case where gold-cyanide complex formation is mediated by a bacterium called *Chromo bacterium violaceum.* (Brandl and Faramarzi, 2006; Campbell *et al.*, 2001; Smith and Hunt, 1985).

2.8 Conclusion from literature review

Tailings from gold mines are a large source of pollution. The scattering of mine tailings dumps without any remediation creates extensive pollution to the soil and streams around the mines. The tailings which are not remediated or covered are easily corroded during rainfall and washed away to neighbouring areas. The mine tailings release toxic metals, which are likely to cause contamination of the environment. Some of the metals are sulphide minerals and such minerals undergo oxidation processes, when combined with rainwater, and cause AMD. Microorganisms in tailings break down and feed on organic matter and release acids (organic and inorganic), which promote the mobility of metals. So industries utilize these microorganisms (heterotrophic and autotrophic microorganisms) to extract metals by a process known as bioleaching. Bioleaching is chosen from among other processes due to the fact that it is an environmentally friendly process and is inexpensive. Mine tailings are managed by adding organic amendments as a cover.

2.9 References

1. Ahmadi A, Khezri M, Abdollahzadeh A.A, Askari M, (2015. Bioleaching of copper, nickel and cobalt from the low grade sulfidic tailings of Golgohar Iron Mine, *Iran. Hydrometallurgy* 154) 1–8.
2. Ata Akcil a,*, Soner Koldas, 2006. Acid Mine Drainage (AMD): causes, treatment and case studies. *Journal of Cleaner Production* 14, 1139-1145
3. Amiria F, Mousavic S.M, Yaghmaeia S., Barati. M, (2012). Bioleaching kinetics of a spent refinery catalyst using Aspergillus niger at optimal conditions.*Biochemical Engineering Journal*. 67, 208– 217.
4. Behera S.K, Sukla L.B and Mishra B.K, 2015. Leaching of nickel laterite using fungus mediated organic and synthetic organic acid.*Mineral Processing Technology*. 946–954
5. Bosecker K, 1997. Bioleaching: metal solubilisation by microorganisms. *FEMS Microbiology*. 20, 591-604.
6. Brandl1 H and Faramarzi M.A, (2006). Microbe-metal-interactions for the biotechnological treatment of metal-containing solid waste. *China Particuology*. 4, 93-97.
7. Campaner V.P, Wanilson Luiz-Silva W and Machado W, 2014. Geochemistry of acid controlling metal attenuation in stream waters, *southern Brazi. Anais da Academia Brasileira de Ciências.* 86, 539-554
8. Cousins C, Penner G.H, Liu B, Beckett P, Spiers G, 2009. Organic matter degradation in paper sludge amendments over gold mine tailings. *Applied Geochemistry* 24, 2293–2300.
9. Coto O, Galizia F, Hernández I, Marrero J, Donati E, (2008). Cobalt and nickel recoveries from laterite tailings by organic and inorganic bio-acids. *Hydrometallurgy*. 94, 18–22.
10. Davies, 2012. Advances in mitigation and rehabilitation technology in major and abandoned mines in Sub-SaharanAfrica. *Czech Geological Survey*. 978-80-7075-781.

11. Deepatana A, Valix M, 2006. Recovery of nickel and cobalt from organic acid complexes: Adsorption mechanisms of metal-organic complexes onto aminophosphonate chelating resin. *Harzadous Materials*. 137, 925-933.
12. Gadd G.M, (2014). Microbial influence on metal mobility and application for bioremediation. *Geoderma* .122, 109– 119.

13. Jain N. and Sharma D.K, (2004). Biohydrometallurgy for Nonsulfidic Minerals—A Review. *Geomicrobiology Journal*. 21, 135–144.

14. Jia y, Maurice C, Ohlander B, 2014. Metal Mobilization in Tailings Covered with Alkaline Residue Products: Results from a Leaching Test Using Fly Ash, Green Liquor Dregs, and Lime Mud. Mine Water Environ.

15. Lee J and Pandey B.D, (2014). Bio-processing of solid wastes and secondary resources for metal extraction – *A review. Waste Management*. 32, 3–18.

16. Liu Y, Zhou M, Zeng G,Wang X, Li X, Fan T, Xu W, (2008). Bioleaching of heavy metals from mine tailings by indigenous sulphur-oxidizing bacteria: *Effects of substrate concentration. Bioresource Technology*. 99, 4124–4129.

17. Liu Y, Zhou M, Zeng G, Li X , Xu W, Fan T, (2007). Effect of solids concentration on removal of heavy metals from mine tailings via bioleaching. *Hazardous Materials*. 141,202–208.

18. Li X, You F, Huang L, Strounina E and Edraki M, 2013. Dynamics in leachate chemistry of Cu-Au tailings in response to biochar and woodchip amendments: a column leaching study.

19. Liefferink, 2011.Assessing the past and the present role of the National Nuclear Regulator as a public protector against potential health injuries: *The West and Far West Rand as case study*

20. Markewitz K, Cabral A.R, Panarotto C.T & Lefebvre G, 2004 Anaerobic biodegradation of an organic by-products leachate by interaction with different mine tailings . *Journal of Hazardous Materials.* 110, 93–104

21. Mendez M.O. and. MaierR.M, 2008.Phytostabilization of mine tailings in arid and semiarid environments-*An Emerging Remediation Technology*.

22. Mishra D, Kim D, Ahn J and Rhee Y, 2005. Bioleaching: A Microbial Process of Metal Recovery; *A Review. Metals and materials Internationa*l. 11, 249-256.

23. Misra V, Tiwari A, Shukla B, Seth C.S, 2009. Effects of soil amendments on the bioavailability of heavy metals from zinc mine tailings. *Environ Monit Assess*. 155, 467–475.

24. Mulligan C.N, Kamali M, Gibbs B.F, (2004). Bioleaching of heavy metals from a low-grade mining ore using *Aspergillus niger. Journal of Hazardous Materials* 110, 77–84.

25. Naicker K, Cukrowsk E, T.S. McCarthyT.S, 2003. Acid mine drainage arising from gold mining activity in Johannesburg, South Africa and environs. Environmental Pollution 122, 29–40.

26. Neuschütz C & Grege M, 2Stabilization of Mine Tailings Using Fly Ash and Sewage Sludge Planted with Phalaris arundinacea L. *Water Air Soil Pollut*. 207, 357–367

27. Nguyen V.K, Lee M.H, Park H.J, Lee J, (2008). Bioleaching of arsenic and heavy metals from mine tailings by pure and mixed cultures of *Acidithiobacillus spp. Engineering Chemistry*. 21,451–458.

28. Oelofse S.H.H, Hobbs P.J, Rascher J and Cobbing J.E, 2007. The pollution and destruction threat of gold mining waste on the Witwatersrand - *A West Rand case study*

29. Oelofse S, 2008. Mine water pollution - acid mine decant effluent and treatment: a consideration of key emerging issues that may impact the state of the environment. *Department of Environmental Affairs and Tourism*.

30. Park J, Han Y, Lee E, Choi U, Yoo K, Song Y, Kim H, 2014. Bioleaching of highly concentrated arsenic mine tailings by *Acidithiobacillus ferrooxidans. Separation and Purification Technology*.133, 291–296.

31. Praburaman L, Park J, Govarthanan M, Selvankumar T, Oh S, Jang J, Cho M, Kamala-Kannan S, ⇑, Oh B, 2015. Impact of an organic formulation (panchakavya) on the bioleaching of copper and lead in contaminated mine soil. *Chemosphere*. 138, 127–132.

32. Santos E.S, Magalhães M.C.F, Abreu M.M, Macías F, 2014. Effects of organic/inorganic amendments on trace elements dispersion by leachates from sulfide-containing tailings of the São Domingos mine. *Time evaluation*. *Geoderma* 226–227, 188–203

33. Seh-Bardan B.J, Othman R, Wahid SA, Husin A, and Sadegh-Zadeh F, (2012). Bioleaching of Heavy Metals from Mine Tailings by *Aspergillus fumigatus*.*Bioremediation Journal*. 16, 57–65.

34. Paul Schwab a, D. Zhu b, M.K. Banks. Heavy metal leaching from mine tailings as affected by organic amendments. *Bioresource Technology*.98,2935–2941.

35. Stoltz E & Greger M, 2006. Release of metals and arsenic from various mine tailings by *Eriophorum angustifolium*. *Plant Soil*. 289, 199-210

36. Vuković M, Štrbac N, Sokić2 M, Grekulović M, Cvetkovski V, (2014). Bioleaching of pollymetallic sulphide concentrate using thermophilic Bacteria. Scientific Paper. 68, 575–583. Debaraj Mishra, Dong-Jin Kim, Jong-Gwan Ahn, and Young-Ha Rhee, 2005. Bioleaching: A Microbial Process of Metal Recovery; A Review. *Metals and Materials*. 3, 249-256.

Wali A, Colinet G & Ksibi M, 2014. Speciation of Heavy Metals by Modified BCR Sequential Extraction in Soils Contaminated by Phosphogypsum in Sfax, Tunisia.

37. Watling, 2006. Review of biohydrometallurgical metals extraction from polymetallic mineral resources. *Minerals*. 5, 1-60.

38. Wang J, Huang Q, Li T, Xin B, Chen S, Guo X, Liu C, Li Y, (2015). Bioleaching mechanism of Zn, Pb, In, Ag, Cd and As from Pb/Zn smelting slag by autotrophic bacteria. Journal of *Environmental Management*. 159, 11-17.

39. Young I,e Renault S, Markham J, 2015. Low levels organic amendments improve fertility and plant cover on non-acid generating gold mine tailings. *Ecological Engineering*. 74, 250–257

40. Zanuzzi A. Arocena J.M, Mourik J.M.V, Cano F, 2009. Amendments with organic and industrial wastes stimulate soil formation in mine tailings as revealed by micromorphology. *Geoderma*. 154, 69–75.

41. Zhong-bing H , Ting L, Yun-guo L, Yu X, Ting-ting L, Hui W, (2014). Influence of sulphur addition/solids content ratio on removal of heavy metals from mine tailings by bioleaching. *J. Cent. South Univ*. 19, 3540–3545.

CHAPTER 3

Article 1

Biological Influence on the Mobility of Metals from Mine Tailings Dump Located in Krugersdorp Area.

This article was written in order to satisfy the main objective, which is stated as follows: to investigate the susceptibility of metals released from tailings dumps with a specific focus on the influence of biological matters on the mobility of metals.

It was found that the mine tailings from the Krugersdorp mining area consist of heterotrophic and autotrophic, species which in certain cases are used in bioleaching. In the sequential leaching results it has been found that in the fractionating of heavy metals, metals from the most tightly bound fraction (residual) are not easily released, but that the metals found in large amounts in the labile fractions, are easily released.

Biological influence on the mobility of metals from mine tailing dump located in Krugersdorp area

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Abstract

Mining activities and smelting of minerals and ores have enhanced the potential of heavy metals in the tailing dumps or solid wastes to mobilize highly after deposition in the environment**.** In nature, microorganisms are documented to mobilize metals from minerals, degrade rocks and also oxidize and reduce metals. Asequential extraction method, according to the Tessier method was used to separate heavy metals into the following six fractions: (F1) water soluble (H_2O), (F2) exchangeable metals, (F3) easily reducible (CO_3), (F4) Moderately reducible fraction (Oxide), (F5) metals correlated with organic materials and sulphides (organics) and (F6) a residual fraction. The results showed higher concentrations of heavy metals such as Fe, Pb and Zn, which were dominant in various fractions of the different sampling points (top, middle and bottom of the tailing dump). The DNA sequencing was carried out on tailing samples to identify the microorganisms likely to promote the mobility of metals. Among the host of microorganisms identified, autotrophic species such as *Leptospirrillum* sp and *Sulfobacillus*, as well as heterotrophic species such as *Bacillus* sp and *Pseudomonas* sp are those frequently reported in bioleaching processes. The binding groups identified by FTIR attest of the presence of organic matters which are likely to be involved in the entrapment of metals in the organic fraction of the tailing dumps.

With most of the metals being attached to the exchangeable and the organic fractions of the tailing dumps, coupled with the presence of active microorganisms, the susceptibility of metal release from the tailings is more probable overtime.

Keywords: Tailing dumps, sequential leaching, microorganisms, mobility of metals, pollution

3.1 Introduction

Anthropogenic activities like mining, and smelting of metal from ore and sulphide ores have increased the availability and accumulation of heavy metals pollution in the ecological system [1].Such activities generate huge amount of wastes which include tailings and waste rocks. [2]. Mine tailings are finely crushed rock particles and mineral wastes remaining after extraction of valuable components that are produced and deposited in slurry form on tailing dumps [3]. Mine tailings can be referred to as a mine soil. In South Africa gold mines constitute more wastes than the other mineral mines, and thus make it the largest source which contributes to pollution and such can be seen from the gold mining area called Witwatersrand basin. [4]. Wastes from such anthropogenic activities release heavy metals which can be leached out to streams, and such metals are found in higher concentrations. Those heavy metals are toxic to the environment and are able to persist for long period in the soil as are unable to be degraded by microorganisms. [5]. The presence of high concentration of toxic metals make the tailings among other mine wastes, the largest environmental impact and the most exposed to wind dispersal and water erosion which are the main mechanisms for the loss of metals from mine tailings [6]. Mineral sulphides like pyrite (FeS_2) tend to cause acid mine drainage (AMD)when they undergo oxidation and such happen when erosion of poorly managed tailings dumps occurs, and the tailings subsequently washed away by rain water [3]. For example, mine tailing found in the abounded mines in the Krugersdorp area have eroded and mobilized to the bottom of the dump and neighbouring area and thus has caused soil contamination in that area. The soil and water contamination by mine tailings of soil and water might results in a high level of toxicity from heavy metals like Zn, As, Pb, Ni Cr and Cu which are mostly found in contaminated areas. The presence of Arsenic in high amounts in mine tailings owes to the fact that it occurs naturally in gold and uranium[7]. Some studies have investigated the availability of metals in the soil and tailings; according to the study reported by Wu et al. [8], the prediction of metal associated bioavailability and mobility is vital. The persistence of metals processes in the soil results into some geochemical factors which are used to fractionate metals.

Biological influence processes can contribute to a large extent to future technologies which includes mine wastes treatment; in this case the microorganisms are accepted to be the natural way of solving the environmental issues [9]. According to such studies microorganisms can enhance the mobility of the metals from its ores or minerals [10]. Microorganisms can be able to influence the mobility of metals by leaching with autotrophic and heterotrophic bacteria and fungi, complexation using microbial materials [11].

Most naturally occurring bacteria and fungi accomplish numerous physiologically important reactions that enable them to grow and reproduce [12].Basically the influence of bacteria and fungi on mobilization of metals from minerals depend on four mechanisms namely: (i) acidolysis, (ii) complexolysis, (iii) redoxolysis, and (iv) alkylation [9,12], those mechanisms allow microorganisms to mobilize metals by forming organic acids, by oxidizing and reducingminerals and by forming chelates[12]. The organic acids are produced by heterotrophic microorganisms, whereas the inorganic acids are produced by autotrophic organisms. The autotrophic microorganisms use CO_2 as a source of carbon and get energy when they oxidize ferrous (Fe^{2+}) to ferric (Fe^{3+}) and thus make it easy for metals to be removed as an acid will be generated and energy obtained for growth from the process of oxidizing which creates acidic conditions favourable for metal removal from soil [13]. Autotrophic bacteria can also be called Sulphur-oxidizing bacteria, as are capable of oxidizing the minerals which can cause the metals to be released [14]. Heterotrophic bacteria and fungi, which need organic carbon for metabolism, are able to leach non sulphudic ores and minerals which do not have any sources for autotrophic bacteria. Heterotrophic bacteria require an organic carbon source as a source of energy and carbon for their growth [15]. The autotrophic bacteria used in bioleaching process to mobilize metals include *Chemolithotrophic* bacteria of genus *Acidithiobacillus and Thiobacillus,* such a*s T. ferrooxidans*, *A.thiooxidans* and *thiobacillusthioparus* [16,13]. The *Chemolithotrophic* bacteria are also called the acidophilic bacteria. Heterotrophic bacteria include *Bacillus licheniformis* and *Bacillus polymyxa*, and fungi species such *Aspergillum niger and penicillium simplissimum*. Fungi species such as *Penicillium simplissimum* and *Aspergillus niger* are used in bioleaching process for the recovery of metals from oxide, sillicate and other industrial wastes [17, 9, 12]. The main objectives of this study is to investigate the susceptibility of metals release from tailing dumps with a specific focus on the influence of biological matters on the metal mobility.

3.2 Methodology

3.2.1 Materials

Mine tailing samples were collected from a mine area located in the Krugersdorp, Gauteng, South Africa. The tailings were sampled from the top 30 cm of the surface at 14 locations spread between the top, the middle and the bottom of the dump, using an auger drill. All samples were dried in the laboratory for 48 hours, passed through 75 µm sieve and crushed before characterization and sequential leaching analysis, the remaining of samples were kept in plastics bags prior to use in the rest of experiment.

3.2.2 Characterization of mine tailings by XRD, XRF and FTIR

The mineralogical composition of the tailings samples were carried out using X-ray diffraction (XRD) analysis. The analysis was conducted by using the powder diffractionprocedure, after making powder by crushing to 75 µm particle sizes. Non-oriented powders were examined on a Philips X'pert MPD diffractometer, at a power of 1.6 kW operating at 40 KV. Major and trace elements of the tailings were analysed by the X-ray- fluorescence spectrometer (XRF) which was carried out with magiX PRO SuperQ Version 4. A rhodium (Rh) anode was utilized in the X-ray tube and conducted at 50 kV and current 125 mA; at power level of 4 kW.

The spectra of binding groups were recorded using theFourier transform infrared (FTIR) spectroscopy(IR-Affinity-IS FTIR spectroscopy from Shimadzu) in order to indicate the functional groups found in the mine tailings. The resolution was set to a 4 cm^{-1} and the operational range was 4000-400 cm^{-1}.

3.2.3 Sequential leaching

Mobilization of metals is heavily dependent on chemical form and binding methods.[18]. Generally sequential leaching is the fractionation of metals in the various solid sample structures.[18]. To better understand the transportation and retention mechanism of elements, 14 tailings samples were selected for sequential leaching: 6 samples were collected on top of the tailing dump, 5 in the middle and 2 at the bottom of the tailings dump. The chemical state of metals and its binding strength were evaluated by a sequential leaching method which has six fractions (F1–F6). The leaching method was adopted from that of Tessier et al. (1979; modified) as cited by Arwidsson and Allard [19]. Fraction 1 (FI) consists of metals which are soluble in water. Fraction 2 (F2) consists of metals which solubilize partially in acidic conditions. Fraction 3 (F3) (easily reducible fraction) represents metals bound to short range - order Fe, Al and Mn (oxy) hydroxides and poorly-crystallised ferric hydroxylsulfates. Fraction 4 (F4) (moderately reducible fraction) consist of metals which are bound to hydroxides and oxysulphate. Fraction 5 (F5) represents metals which are bound with organic matter and sulphides. Fraction 6 (F6) consists of metals which are bound to sulphides and not easily released. The following leaching scheme was used:

Fraction 1.Water-soluble fraction One gram of tailings sample was added to 20 mL of water; the concoction were shaken in the shaker without any interruption for15 min at 20°C. After 15 min of shaking the mixture were then centrifuged at the speed of 1600 rpm for 20 minutes. The supernatant was stored for analysis of released elements using the inductively coupled plasma optical emission spectrometry (ICP-OES). The same procedure of centrifugation and analysis was used in each fraction after shaking.

Fraction 2. **Exchangeablefraction.**The surplus F1 were mixed with 20 mL of 1.0 M NH_4Ac where by the pH was maintained to7.0 by using acetic acid; it was then shaken continuously for an hour at 20°C.

Fraction 3.Carbonatefraction. The leftovers from F2 were mixed with 20 mL of 1.0 M NH_4A at pH of 5 maintained the addition of acetic acid , then such concoction were shaken at 1600 rpm for 5 h at 85°C.

Fraction 4.Oxide fraction.20 mL of 0.043 M$NH_2OH–HCl$ was added to the F3 residue with acetic acid, the concoction were shaken at 1600 rpm for 5 h at 85°C.

Fraction 5. Organicfraction. 12 mL of 0.02 M HNO_3, 30% H_2O_2 (3:5 v/v were added to the residue from F4 at pH of 2.0), then the mixture were shaken continuously at 1600 rpm for 3h at 85°C, of 7.5 mL of 3.2 M NH_4Ac in 20% $HNO_3$and 10.5 mL H_20 were added, then it was shaken again for 30 min at 20°C.

Fraction 6. Residual fraction. The kept residue from F5 was added to 10 mL of concentrated $HNO_3$and deionised water of 10 mL.

3.2.4 DNA sequencing

Fresh samples from the abounded mine in Krugersdorp area were used for DNA sequencing. The samples were divided into 3 according to the site of collection as follows: top, middle and bottom of the dump. Genomic DNA was extracted from 1 g of each of the 14 tailings samples by using ZR soil microbe DNA Mini Prep Kit. Such DNA was removed from mine tailings samples. Its concentrations were determined by using a spectrophotometer integrated to a Nano-Drop spectrophotometer (Thermo scientific). The DNA extracted materials were sequenced by using Next Generation Sequencing (NGS).

3.2.5 Determination of organic carbon

1. The organic carbon content in the tailings was determined by the use of oxidation method called Walkley-Black chromic acid 2 g of tailings were added into 10 mL of 1 N $K_2Cr_2O_7$then shaken by hand in order to ensure the full saturation of a sample in the solution. 20 mL concentrated H_2SO_4 were then put in the mixture after saturation, then heated to temperature of 135 °C. The mixture was allowed to cool for 20 minutes. The same procedure was followed for two blanks (without soil) in order to normalize the

$FeSO_4$solution. After cooling, 200 mL distilled water was added, the titration with $FeSO_4$ was done with the indicator called ferroin. The titration was conducted as follows:

"Ferroin" Titration

Few drops of ferroin were added to the mixture, then titration was done with 0.4 N $FeSO_4$. The end point was indicated by greenish colour and then dark green colour later on. At this point, the ferrous sulphate was re-approached drop-by-drop until the colour changed sharply from blue-green to reddish-grey. About 1.0 mL of 1 N $K_2Cr_2O_7$ was added and the end point was reached after adding about 10mL, then the experiment was repeated using decreased mass of tailings sample.

3.3 Results and discussion

3.3.1 Characterization of mine tailings

3.3.1.1 XRD

The mineralogical composition of the 14 representative samples used in this study is summarized in Table 1. The mineralogical composition of tailing samples from the Krugersdorp mining area was analysed by X-ray diffraction (XRD). The XRD structure showed the dominance of quartz (SiO_2) minerals in the top and middle of the tailing dump, while other minerals, such as iron catena-silicate & ferrosilite, sillimanate, and aluminium iron (III) oxide were only detected in high concentration in few samples. A similar trend about the dominance of quartz in the tailings was reported in the study by Novhe et al. [20].

Table 1: Mineralogical composition of tailing samples

Minerals	Weight percentage in each sample													
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Quartz	84.8		-	91	79	85	92.3			97	73.2	91	-	-
Iron catena-silicate, ferrosilite	-	96	-	-	-	-	-	-	-	-	-	-	-	-
Aluminium iron(III) oxide	-	-	-	-	-	-	-	60	-	-	-	-	-	
Sillimanite	-	-	-	-	-	-	-	-	-	-	-		85	-
Dialuminum silicate oxide, kyanite	-	-	95	-	-	-	-	-	-	-	-	-	-	-
Dicalcium silicate	-	-	-	-	-	-		-	-	-	-	-	-	87

3.3.1.2 XRF

The major, minor and trace elements were determined by using XRF analysis, represented in Table 2. SiO_2 is the dominant oxide in all samples collected from the Krugersdorp mining area, which ranges from 40.49% to 89.15%. This confirms the result obtained using the XRD technique. SiO_2 was also found by others to have dominion over other oxides in mine tailings [20]. Heavy metals such as Al, Fe, Cr, Ni, Zn, Cu, As, Pb and Co were also identified in the tailings samples; however, only Cr, Fe, Pb and Zn were present in almost all the samples and were therefore considered as main focus in the rest of the study.

Table 2: Major and trace elements in tailing samples

Samples	**Mass %**				
	Cr_2O_3	**Fe_2O_3**	**PbO**	**ZnO**	**SiO_2**
1	0.101	7.076	0	0.014	69.683
2	0.054	2.677	0.015	0	81.366
3	0.083	3.026	0	0	78.139
4	0.07	1.792	0	0.006	80.707
5	0.081	2.901	0.009	0.006	78.024
6	0.063	2.702	0.065	0.007	78.55
7	0.109	1.894	0.017	0.007	86.478
8	0.113	5.58	0.03	0.008	72.772
9	0.075	38.201	0.331	0.028	40.485
10	0.055	6.183	0.211	0.014	69.741
11	0.019	10.472	0.039	0	70.166
12	0.066	6.761	0	0.006	75.346
13	0.048	0.997	0	0	89.152
14	0.069	7.235	0	0.103	41.977

3.3.1.3 FTIR

The FTIR results for the samples taken at the top of the dump (S1-S7), middle (S8-S12) and bottom of the tailing dump (S13-S14) are shown in Figure 1A, B and C respectively. Generally, the spectra which depict the top and the middle of the dump were very similar and exhibited same peak pattern. However, most samples from the top of the dump do not show the broad peak identified in the samples from the middle of the dump, which is about 2400 cm^{-1} due to stretching hydrogen bonded OH group. Samples from the middle of the dump also exhibit a peak which range between 1609.85 and 1424.70 cm^{-1} which corresponds to the H-CH bond, as well as a peak in the range 1124-1000cm^{-1}, which is attributed to C-O stretching, i.e. esters and ethers. Samples from the bottom of the dump reveal peaks at 3029.03-2917.65 cm^{-1}, 2393.33-2240.33 cm^{-1} and 1083.31-1014.25 cm^{-1}, which are attributed to H-C-H asymmetric and symmetric/ H-C-H asymmetric stretching, C=H-H asymmetric ,C≡N and C-O stretching. All the groups identified on the spectra are able to bind to metals. The organic matters normally are likely to complex as a ligand and release the metals. In that regard Brandl and Faramarzi, [9] have explained the mechanism of complexolysis in which the microorganisms complex with metals or use the chelating agents which results in the metals mobility, such complexes are able to detach the bound metals from the surface. Although these metals can mobilize or release metals from tailings, the availability of metals in solution can be affected by the binding group identified by FTIR, all the C2 report can bind to the metals and prevent the release of metals. The groups observed by FTIR analysis are similar to the groups causing metal mobility as reported by Brandl and Faramarzi [9], namely carboxyl, sulfonate, phosphate, hydroxylamino or imino residues.

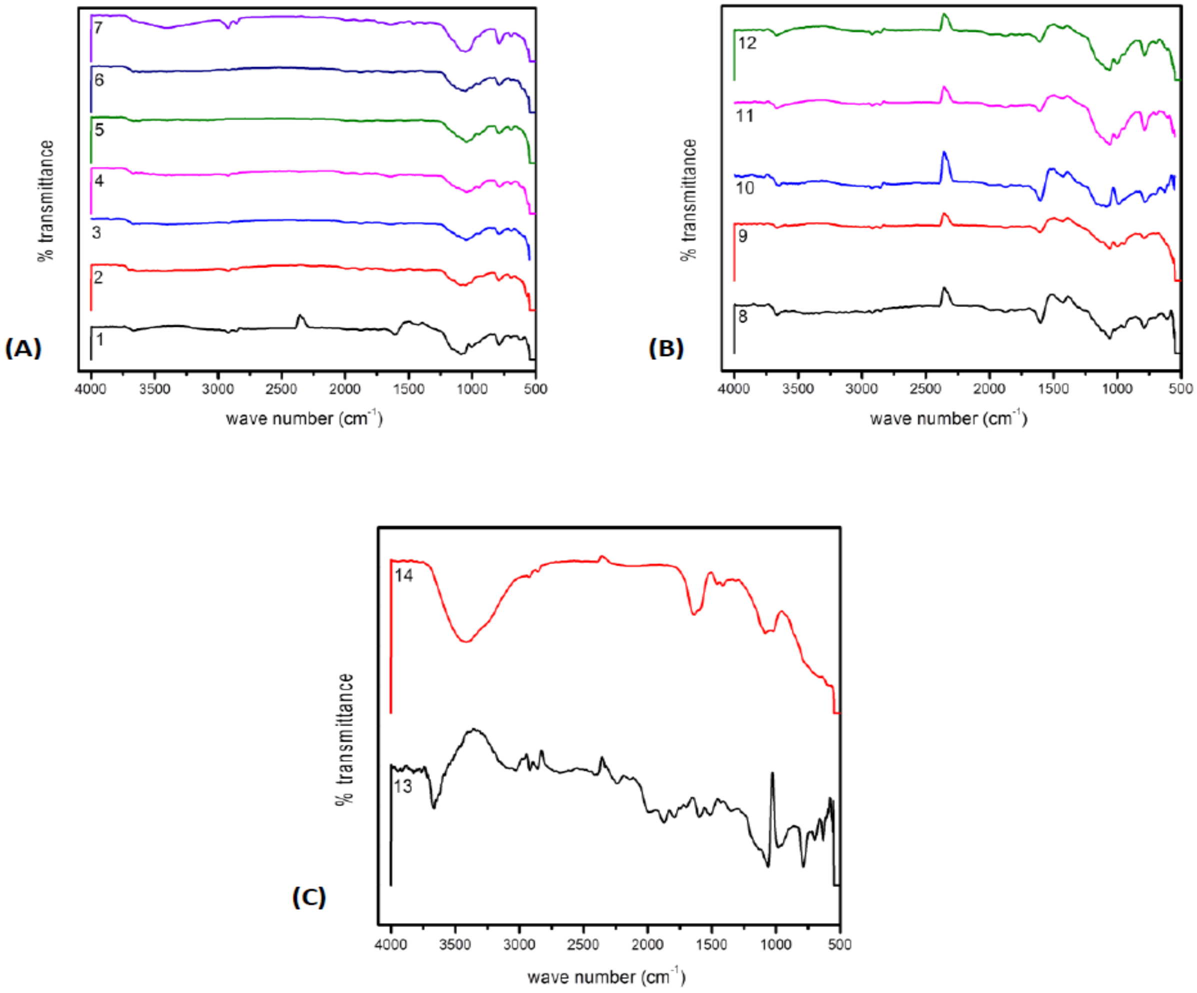

Figure 1: FTIR spectra of (A) top samples 1-7, (B) middle samples 8-12 and (C) bottom samples 13-14 of the tailing dump

3.3.2 Microorganisms in the tailing dumps

In the DNA sequencing results shown in Table 3, the acidophile bacteria of genus *Leptospirillum ferroxidans* were found in all the three sampling sites and represented 0.14%, 0.36% and 0.01% of all the microorganisms in samples from the top, middle and bottom of the dump, respectively. The acidophile bacteria of genus *Sulfobacillus* sp were also found in the middle of tailing dumps. According to the literature these microorganisms often occur in dump of mine waste rock and talings from sulfide ore. Acidophilic iron(II)- and sulfur-oxidizing bacteria excrete sulphuric acid whichfacilitates in the process of metal removal from the mine waste[21]. Heterotrophic bacteria were represented by *Bacillus* sp and *Pseudomonas* sp which are among the bacteria species most likely to degrade the organic matter to form organic acids; these species were found at all the sampling sites.

Table 3: Selected species from blast output results

Sampling Site	**Autotrophic bacteria**		**Heterotrophic bacteria**	
	Species	**%**	**Species**	**%**
Top	*Leptospirillum*	0.14	*Bacillus*	1.6
			Pseudomonas	1.91
Middle	*Leptospirillum*	0.36	*Bacillus*	1.33
	Sulfobacillus	0.1	*Pseudomonas*	1.1
Bottom	*Leptospirillum*	0.01	*Bacillus*	0.06
			Pseudomonas	1.22

3.3.4 Mobility of metals

The results obtained in the various steps of the leaching technique are shown in Table 4 and figure 2. In the water soluble fraction (F1), Zn is the most abundant metal and ranges between 0 - 60.7% for samples taken from the top of tailing dump (S1, S2, S3, S4, S5, S6, S7), whilst it ranges between 0 to 62.5% for the sample taken from the middle of the dump (S8, S9, S10, S11, S12) and it shows a low percentage for samples collected from the bottom of the dump, in the range between 0 - 2.7%. The abundance of Zinc in the residual fraction (F6) ranges from 0 to 30.8% for the tailing samples collected from the top of the tailing dump and for sample taken from the bottom of the dump it ranges from 0 to 23%. The lower recovery from the samples collected at the bottom layer was likely due to the fact that these samples were mostly sulphide minerals, which do not dissolve easily. The recovery percentage of zinc in other fractions was low, which means that the mobility of Zn in the tailing is much likely to occur in the exchangeable fraction while the rest is more likely to remain in the tailing for a long time. The metals leached in—‘‘water-soluble’’ fraction (i.e. leaching stage 1)—are easily released as are not tightly bound to the surface and may be potentially bioavailable and mobilized highly [22]. Elements found in this fraction solubilize easily, so if metals are most abundant in this fraction, then it means that they are likely to contaminate the environment [22].

The highest recovery of Pb bound to the carbonate fraction (F3), was found in samples collected at the top of the tailing dump and ranged from 0 - 85.65%, which was higher as compared to the residual fraction and the other four fractions in which its concentration ranged from 0 to 34.37%. Pb in the fraction collected at the top of the tailing dump has a relatively higher mobility and potential bioavailability than the residual fraction and the other phases (F4 and F5). The reducible or bound to organic fraction has a higher concentration of Pb than the other geochemical phases, which means that Pb is less likely to be released under environmental conditions. According to the XRF results there was no Pb in the samples collected at the bottom of the dump, which explains why no recovery was achieved through sequential leaching.

Fe was mainly recovered at the bound to organic fraction for the sample taken from the middle of the dump, ranging from 0 to 88%. In this fraction the Fe recovery % is higher than in the residual and all other fraction for samples collected from the same site, which means that this metal is mostly located in the organic fraction. Metals which are found in higher concentrations in the residual fractions are less likely to pollute the environment [23].

Fe is more abundant if bound to a carbonate fraction (F3) and for the sample found at the top of the dump the Fe recovery % is higher than in the other fractions for the samples collected from the same site. The Fe recovery % is high for samples taken from the bottom of the dump in the fraction bound to a carbonate, and ranged from 8.34 to 10.09%. The recovery % of Cr is relatively low in all fractions, however the water soluble fraction (F1), exhibits a high concentration for the sample found on top of the dump as the recovery ranges from 0 - 1.58%. Thus this recovery % is the highest compared to all the other phases, considering samples collected from the same site. For the samples collected in the middle of the tailing dump Zn was the metal easily removed in all the fractions; however higher recovery of Zn was achieved in fraction 1 where the recovery percentage ranged between 0 and 62.51 %; implying that under environmental conditions, Zn will be very mobile from the middle layer of the tailings.

The microorganisms can extract metals by using the sequential extraction method, as they use organic acids and inorganic acids to release a metal which is the same trend in this process. According to Wali et al [24], the exchangeable fraction which is a non-resistant fraction is used by microorganisms. The order of recovery of the other metals mostly varied according to the specific sites in the middle layer; however, according to the general trend, the following order Fe > Pb > Cr could be considered. The recovery of metals in the samples from the bottom of the tailings was poor compared to the other sites, which furthermore confirms the fact that the refractory structure or mineralogy of the samples from the bottom of the tailings is a limiting factor to the mobility of the metals. It is therefore clear that the oxidation (weathering) of the top surface of the tailing which is more exposed to atmospheric conditions contributes to increase the mobility of metals.

Table 4: Sequential leaching results showing six fractions in a three sampling sites: Top of the tailing dump (S1-S7), middle of the tailing dump (S8-S12) and bottom & foot of dump (S13 and S14)

Fractions and elements	**% Recovery of metals per sample**													
Fraction 1	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Cr	0.97	0.4	1.04	**1.58**	0	0.19	0.22	0.54	7.23	2.76	0	0.45	0.98	0.08
Fe	0.2	5.15	7.17	0.07	0.34	0.1	0	2.62	20.37	0.08	0.01	0.1	0.02	0.06
Pb	3.59	0	27.5	0	0	19.91	6.85	0.93	0	4.1	0.84	0	0	0
Zn	60.7	0	17.14	57.18	36.7	13.37	18.35	22.77	30.81	62.51	0	**57.44**	0	2.65
Fraction 2	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Cr	0.34	0	0	0.05	0.33	0	0.46	0.03	0.1	0.12	0.06	0	0	0.08
Fe	0.02	0.03	0.13	0,02	0.03	0.12	0.04	0.27	2.98	0.02	3,75	9.25	0.02	0.14
Pb	4.19	0	0	0	0	34.15	6.05	6.2	0	0	4.2	**62.28**	0	0
Zn	10.38	0	8.34	0	24.37	0	7.98	11.77	0	0	0	0.48	0	5.31

Fraction 3	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Cr	1.19	0.05	0.11	0	0.05	0	0.89	0.1	0	0.15	0.09	0.81	0.07	0.12
Fe	0.17	0.14	20.93	8	0.04	0.14	0.23	3.21	16.85	3.48	0.03	0.09	8.34	10.09
Pb	0.07	0	**85.62**	0	0	0	0	0	0	14.69	2.93	0	0	0
Zn	47.91	0	19.97	26.75	32.42	0	9.58	8.07	5.53	11.07	0	40.91	0	0.81
Fraction 4	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Cr	0.15	0.05	0	1.02	0	0.06	0.19	0	0.08	0.15	0.09	0	0	0
Fe	2.21	2.64	62.11	11.74	49.45	0.52	0.23	5	1.52	0.03	0.85	5.56	0.09	2.5
Pb	17.11	0	0	0	0	39.4	6.25	5.32	1.46	12	3.7	73.04	0	0
Zn	8.7	0	23.13	0	50.67	3.85	11.9	0	44.26	7.46	0	19.12	0	3.62
Fraction 5	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Cr	0.43	0.4	0.3	0.44	0.19	0.59	0.55	0.42	0.39	0.37	0	0.61	0.33	0
Fe	2.03	3.68	7	0.54	0.05	1.89	1.34	0.28	**88.1**	2.64	0.73	4.02	0.02	4.4
Pb	8.13	0	68.02	0	0	0	0	0	0	13.82	0	70.56	0	0
Zn	7.47	0	10.41	0	24.41	0	12.21	6.76	13.91	0	0	23.92	0	2.51
Fraction 6	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Cr	0.14	0.5	0.52	0.75	0.62	0.71	0.8	0.69	0.73	0.11	0.04	0.55	0.6	0.14
Fe	0.2	0.85	2.43	0.41	0.96	0.39	0.54	0.16	10.16	0.34	0.12	0.23	0.11	0.47
Pb	0	0	0	0	0	34.37	9.78	2.07	0.38	0	2.84	50.91	0	0
Zn	11.99	0	14.25	24.93	30.78	2	6.43	0	6.82	13.97	0	23.02	0	0

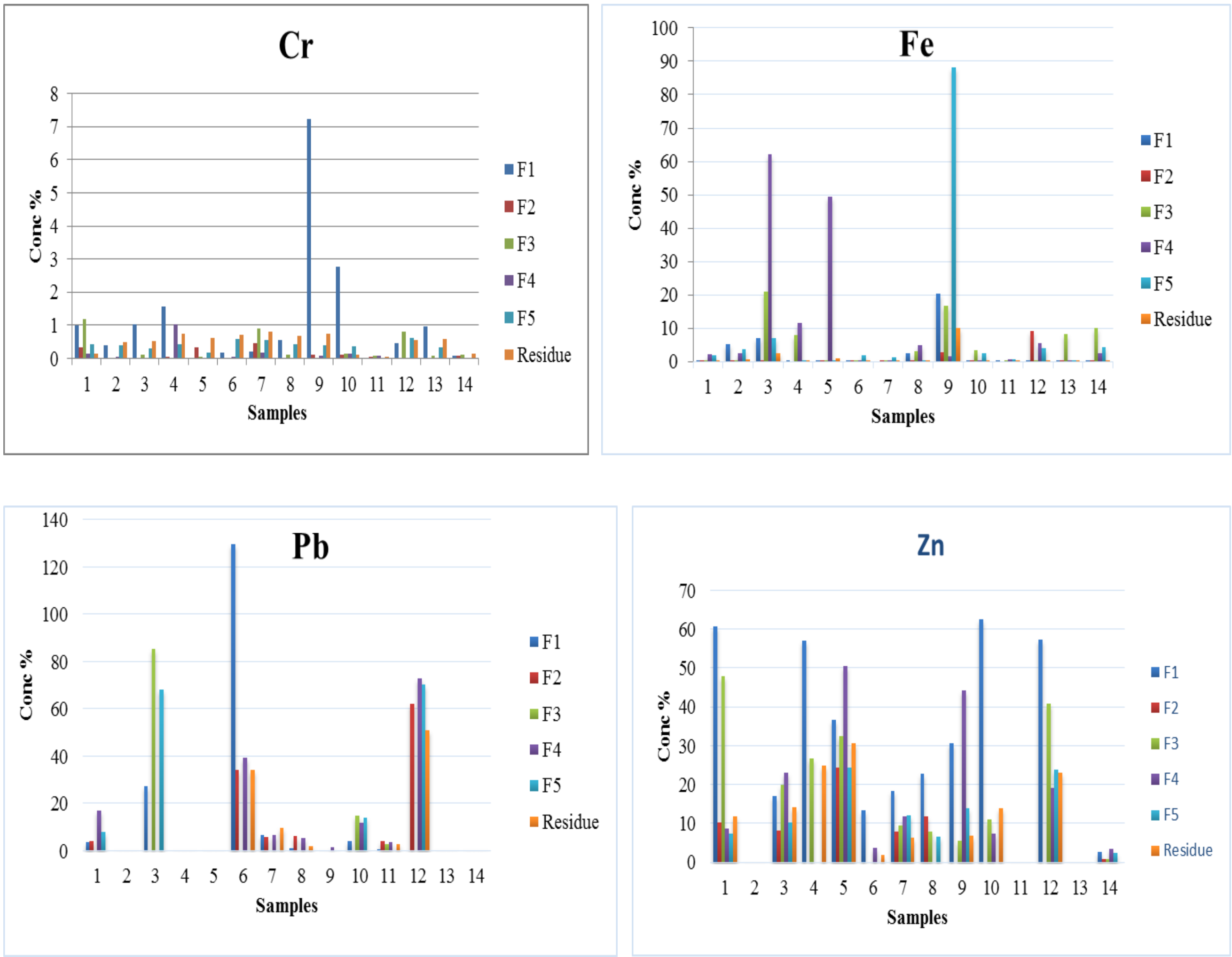

Figure 2: Sequential leaching results showing six fractions in a three sampling sites: Top of the tailing dump (S1-S7), middle of the tailing dump (S8-S12) and bottom & foot of dump (S13 and S14

3.3.5 Organic carbon (OC) content

The organic carbon results are summarized in Table 5. Organic carbon was present in all samples, i.e. collected on the top of the tailing dump (S1, S2, S3, S4, S5, S6, and S7); in the middle of the dump (S8, S9, S10, S11 and S12) and also at the bottom of the tailing dump (S13 and S14). The top and the middle of the tailing dump contained OC in the range of 0.06% to 1.44% while the bottom of the tailing dump exhibited a relatively lower concentration of OC in the range of 0.09% to 0.18%. However the organic carbon was mainly found in sample S7 which is the sample collected at the top of the dump and S12 which taken at the middle of the dump. The organic carbon acts as the source of nutrients for microorganisms [24], so the presence of organic carbon in all three sampling sites may contribute to the mobility and/or bioavailability of metals, as the microorganisms are capable of degrading the organic carbon to form organic acids which promote the dissolution of metals from tailing dumps [25].

Table 5: Organic carbon (OC), top of the dump (S1-S7), middle of the dump (S8-S12) and bottom of the dump (S13-S14)

Samples site	**OC (%)**
1	0.19
2	0.2
3	0.06
4	0.09
5	0.06
6	0.06
7	1.44
8	0.13
9	0.09
10	0.08
11	0.06
12	1.44
13	0.09
14	0.18

3.4 Conclusion

The mineralogical structure showed that the top and middle layers of the tailing were mostly made up of oxide minerals while the bottom layer contained sulphide minerals. Metals of commodity values but also with potential of toxicity were found in the tailing dump, irrespective of the layer. It was found that the mineralogical structure of the tailings had a significant impact on the mobility of the metals as they were mostly mobile in the top and middle layers, which were made of oxide minerals while they show poor mobility in the samples from the bottom layer, made up of sulphide minerals. The speciation results have shown that most of metals considered in this study were released in large amount from the mobile fractions such as water soluble, carbonate fraction and organic fractions than from the residual fractions, which indicate that these metals are likely to be mobilized in the environment. Autotrophic and heterotrophic microorganisms identified in the tailing dumps have the potential to mobilise metals through mechanisms such as acidolysis or complexolysis; considerable amount of organic carbon was measured in the tailings which can sustain the growth of heterotrophic microorganisms while forming organic acids as by-products. Binding groups such as H-C-H, C=H-H,C≡N and C-Ofound in the tailings are prone to participate in the entrapment of metals in the organic fraction. The susceptibility of metal release from the tailing dumps is therefore likely to be stimulated by chemical and biological mechanisms that can occur naturally in the environment.

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References

1. Rodrı´guez L., Ruiz E., Alonso-Azca´ J., Rinco´n J. Heavy metal distribution and chemical speciation in tailings andsoils around a Pb–Zn mine in Spain. Journal of Environmental Management. **90**, 1106–1116 (2009).

2. Lim M., Han G., Ahn J., You K., and Kim H. Leachability of arsenic and heavy metals from mine tailings of abandoned metal mines. Environ Res Public Health. Nov; 6(11), 2865–2879 (2009).
3. Ndasi M.B. The accumulation of heavy metals in sedimentary deposits in the Fleurhof and Russel stream dams of the central rand, Johannesburg. MSC Thesis. (2007).

4. Oelefse S.H.H., Hobbs P.J., Rascher J. and Cobbing J.E. The pollution and destruction threat of gold mining waste on the Witwatersrand - A West Rand case study. (2007).

5. Bakatula E.N., Cukrowska E.M. and Tutu H. Biosorption of metals from gold mine wastewaters by *Penicillium simplicissimum* immobilized on zeolite: Kinetic, equilibrium and thermodynamic studies.Czech Geological Survey, ISBN 978-80-7075-781-9 (2012).

6. Lee S.H., Ji W.H., Lee W.S., Koo N., Koh I.H., Kim M.S., Park J.S. Influence of amendments and aided phytostabilization on metal availability and mobility in Pb/Zn mine tailings. Journal of Environmental Management. **139**: 15-21 (2014).

7. Kwon J.M., Yang J., Lee S., Lee G., Ham B., BoyanovM.I., Kemner K.M., O'LoughlinE.J. Geochemical characteristics and microbial community composition in toxic metal-rich sediments contaminated with Au–Ag mine tailings.Journal of Hazardous Materials. **296**: 147–157 (2015).

8. Wu S.C., Luo Y.M., Cheung K.C., Wong M.H. Influence of bacteria on Pb and Zn speciation, mobility and bioavailability in soil: A laboratory study. Environmental Pollution. **144**: 765-773 (2006).

9. Brandl1 H. and Faramarzi M.A. Microbe-metal-interactions for the biotechnological treatment of metal-containing solid waste.China Particuology. **4**: 93-97 (2006).

10. Ledin M. and Pedersen K. The environmental impact of mine wastes - Roles ofmicroorganisms and their significance in treatment ofmine wastes. Earth-Science Reviews. **41**: 67-108 (1996).

11. Gadd G.M. Microbial influence on metal mobility and application for bioremediation. Geoderma. 122: 109– 119 (2004).

12. Bosecker K. Bioleaching: metal solubilisation by microorganisms. FEMS Microbiology. **20**: 591-604 (1997).

13. Park J., Han Y., Lee E., Choi U., Yoo K., Song Y., Kim H. Bioleaching of highly concentrated arsenic mine tailings by *Acidithiobacillus ferrooxidans*. Separation and Purification Technology. **133**: 291–296 (2014).

14. Coto O., Galizia F., Hernández I., Marrero J., Donati E. Cobalt and nickel recoveries from laterite tailings by organic and inorganic bio-acids. Hydrometallurgy. **94**: 18–22 (2014).

15. Jain N. and Sharma D.K. Biohydrometallurgy for Nonsulfidic Minerals—A Review. Geomicrobiology Journal. **21**:135–144 (2004).

16. Nguyen V.K., Lee M.H., Park H.J., Lee J. Bioleaching of arsenic and heavy metals from mine tailings by pure and mixed cultures of Acidithiobacillus spp. Engineering Chemistry. **21**: 451–458 (2008).

17. Lee J. and Pandey B.D. Bio-processing of solid wastes and secondary resources for metal extraction – A review. Waste Management. **32**: 3–18 (2014).

18. Lu J., Alakangas L., Wanhainen C. Metal mobilization under alkaline conditions in ash-covered tailings. Journal of Environmental Management. **139**: 38-49 (2014).
19. Arwidsson Z. and Allard B. Remediation of metal-contaminated soil by organic metabolites from fungi II—metal redistribution. Water Air Soil Pollut. **207**: 5–18 (2010).

20. Novhe N.O., Yibas B., Netshitungulwana R. and Lusunzi R. Geochemical and minerological characterization of mine residue deposits in the Komati/Crocodile catchment, South Africa: an assessment for acid/alkaline mine drainage *ISBN*. 978-7-5646-2437-8 (2014).

21. Korehi H., Blöthe M.,Sitnikova M.A.,Dold B.and Schippers A. Metal Mobilization by Iron- and Sulfur-Oxidizing Bacteria in aMultiple Extreme Mine Tailings in the Atacama Desert, Chile. Environ. Sci. Technol. **47**: 2189−2196 (2013).

22. Nurmesniemi H., Poykio R., Peramaki P., Kuokkanen T., 2005. The use of a sequential leaching procedure for heavy metal fractionation in green liquor dregs from a causticizing process at a pulp mill. Chemosphere. **61**: 1475–1484 (2005).
23. Ashraf M.A., Maah M.J. and Yusoff I. Chemical Speciation and Potential Mobility of Heavy Metals in the Soil of Former Tin Mining Catchment**.** The Scientific World Journal. (2012).
24. Wali A, Colinet G & Ksibi M, 2014. Speciation of Heavy Metals by Modified BCR Sequential Extraction in Soils Contaminated by Phosphogypsum in Sfax, Tunisia
25. Edwards J.H., Wood C.W., Thurlow D.L. and Ruf M.E. Tillage and crop rotation effects on fertility status of a Hapludalf soil. Soil Sci. Soc. Am. J. **56**: 1577-1582 (1999).

26. Sherene T. Mobility and transport of heavy metals in polluted soil environment. Biological Forum — An International Journal. **2**(2): 11, 2-121.

CHAPTER 4

Article 2

Mobility of metals from mine tailings using different types of organic acids: Batch leaching experiment

This paper addresses organic acids impact on the mobility of metals from mine tailings. The study was conducted in order to satisfy the following objectives:

- To determine the influence of organic acids on the removal of heavy metals.
- To determine the susceptibility of heavy metals release from tailing dumps under different environmental conditions.

The results were as follows:

Oxalic and citric acids were more efficient leaching agents than the other organic acids. The acids were very effective for the mobilization of Al and Fe; both acids achieved high leaching rates within the initial hour of contact. The mobility of metals was high under acidic condition. Increasing concentration of organic acids caused an increase in the concentration of metals, thus also distributed the metals very much. The mobility of metals was also increased at high temperature than at low temperature.

Mobility of metals from mine tailings using different types of organic acids: Batch leaching experiment.

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Abstract

The presence of toxic metals in mine tailings is a major concern because they are hazardous to ecological system and human health. Hence the mobility of heavy metals is an important factor to look at when assessing risk of pollution or contamination in tailing dump. This study was carried out in order to determine the effect of organic acids on the mobility of metals from mine tailings. Characterization of mine tailings was carried out using XRD and XRF. Batch leaching experiment under different initial pH, contact time, temperature, and concentration was carried out in this study. The results show that Fe and Al were the major elements, whereas quartz minerals were considered as the major constituents in the tailing. The batch leaching studies indicated high mobility of elements at low pH, short exposure time, high concentration of organic acids and high temperature. Increase of temperature resulted to faster release of metals, with maximum concentrations of Fe and Al recorded at 48 hours. Oxalic acid and citric acid were found as best leaching agents. The kinetic studies allowed predicting that the dissolution of metals from tailing samples was mostly diffusion controlled.

Keywords: Mine tailings, batch leaching, organic acids, mobility of metals, pH, temperature, concentration.

4.1 Introduction

The utilization of mineral resources it brings important resources, but heavy metals contaminations in the soil and water has become one of the environmental problems within the vicinity of mines (Ding *et al.*, 2014; Conesa and Schuling, 2010). Mining operations introduce various heavy metals into the soil and water. Heavy metals which are toxic to the environment are not degraded and can persist in the environment for a long period of time (Wuana *et al.*, 2010). These metals are released from mine wastes.

South Africa produces an estimated 468 million tons of mineral wastes (Oelefse *et al.*, 2007), and most of it is produced by gold mines accounting for 221 million tons or 47% of all mineral wastes produced per year, making it the largest source of pollution. Among all the wastes, mine tailings are known to be the main environmental effect (Conesa *et al.*, 2007; Dudka and Adriano, 1997) because of its low pHs (Wong *et al.*, 1998; Conesa *et al.*, 2007).

Detoxification of the mine tailings is required to protect the ecological system (Seh-Bardan *et al.*, 2012). Metals were removed from soil by the use of conventional methods such as chemical and physical methods and venting incineration in order to decontaminate it (Praburaman *et al.,* 2015). This convectional mineral process recently used to recover metals, but these metals have disadvantages such as high costs, long repair cycle and low efficiency (Zhong-bing *et al.*, 2011; Dong *et al.*, 2011). In comparison to the conventional methods, bioleaching is a productive process due to the fact that it is not hazardous to the environment, inexpensive and it is easily manageable (Dong *et al.*, 2011). Bioleaching is the use of microorganisms to convert elements from solid to extractable elements which is water soluble by passing water through it" (Brandl, 2001; Mishra *et al.*, 2005; Brandl and Faramarzi, 2006). Mobility of metals in soil or tailings by microorganisms occurs through the use of autotrophic and heterotrophic metabolites and creation of vitalization by methylation (Mishra and Rhee, 2014). Microbes action on metals is based on three principles namely acidolysis, complexolysis and redoxolysis (Brandl and faramarzi, 2006). In these processes/ mechanisms microorganisms are capable of mobilizing metals by the inorganic acids or organic acids they form. For complexolysis processes, the solubilization of metal is by the mechanism which involve the formation chelating or complexing agents which increases the metal mobility (Mishra and Rhee, 2014).

Organic acids can provide protons and anion which complex with metals (Gadd, 2004). Citrate forms complexes with the ions of a metal, for example copper, zinc and highly mobile complexes may be resistant to biodegradation (Gadd, 2001). The reason why this low molecular weight (LMW) anion works as organic ligand, is because of its ability to promote the mobility of heavy metals by complexing with metals, take out the metals from contaminated soil by the ligand exchange reaction (McColl and Pohlman, 1986; Pohlman, 1986; Stone, 1988; Banks *et al* 1994; Burckhard *et al.*, 1995; Kim *et al.*, 2013). Such anions are capable of enhancing the removal of metals from soil. Most studies have focused on the impact of organic acids on the mobility of metals from soils and sediments, however there is less information regarding their release from mine tailings and there is a need to confirm such findings in South Africa as this type of studies have been done in other countries. In this study batch leaching process was applied using organic acids in order to assess the mobilization of metals from mine tailings. Hence the objective of this study is to determine the effects of contact time, temperature, pH and concentration on the mobilization of metals from tailing dumps by organic acids.

4.2 Materials and methods

4.2.1. Sample collection

About 14 mine tailings samples were collected from an abounded gold mine located in the Krugersdorp area, South Africa. The tailings samples were taken from the top 30 cm of the surface using an auger drill. For this study tailing samples used were the representative from the top of the tailing dump (S2) and from the bottom of the tailing dump (S13). All samples were air dried in the laboratory for 2 days, ground in to fine form, sieved through 75 µm to a powder form. Samples in the powder form were used in the entire batch leaching experiment, the remaining of samples were kept in plastics bags prior to use in the rest of experiment.

4.2.2. Batch leaching experiment

Batch leaching test was conducted in order to investigate the influence of organic acids (malic, gluconic, oxalic, and citric acid) on the mobility of metals, such as Fe and Al from contaminated tailing at different concentrations of organic acids (1, 10, and 100 mM) and initial pHs (3.5, 4.5, 5.5, and 6.5) and temperatures (30°C, 40°C and 50°C). In all the experiments, one representative sample from the top (S2) and one from the bottom (S13) of the dump, was used. The experiments were conducted as follows:

4.2.2.1 Effect of time

A mass of 2.5 g of tailing was added to 25 mL of 3 mM organic acid (malic, gluconic, oxalic, and citric acid). The experiment was conducted in duplicate. The mixture added into volumetric flasks were shaken by hand for 1 minute to bring saturation of the tailing with the acid and water and then shaken on orbital agitator at the speed of 200 rpm 25°C for 8, 20, 40 and 48 hours. The pH was measured after shaking and then the samples were centrifuged for 10 minutes at 4000 rpm, then the supernatant was kept in a fridge before analysis. The samples kept in a fridge were then analysed for heavy metals using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Agilent Technologies, USA).

4.2.2.2 Effect of pH

A mass of 2.5 g of tailing was added to 25 mL of 3 mM organic acid (oxalic, and citric acid) and initial pHs (3.5, 4.5, 5.5, and 6.5). The experiment was conducted in duplicate. The pH was kept at desired value with HCl and NaOH. The mixture was added into volumetric flasks then agitated on orbital shaker at room temperature for 24 hrs at 200 rpm. The pH was measured after shaking, then the samples were centrifuged at the speed of 4000 rpm for 10 minutes then the supernatant was kept in a fridge before analysis. The samples kept in a fridge were then analysed for heavy metals.

4.2.2.3 Effect of concentration

A mass 2.5g of tailing was added to 25mL of 1mM, 2mM, 3mM and 4mM organic acid (oxalic, and citric acid) at various concentrations of organic acids (1, 2, 3 and 4 mM).The experiment was conducted in duplicate The mixture was added into volumetric flasks and then shaken on orbital shaker at room temperature for 24hrs at 200rpm The pH was measured after shaking and then the samples were centrifuged for 10 minutes at 40rpm, then the supernatant was kept in a fridge before analysis. The samples kept in a fridge were then analysed for heavy metals.

4.2.2.4The effect of temperature

A mass of 2.5 g of tailing was added to 25 mL of 3 mM organic acid (oxalic and citric acids). The experiment was conducted in duplicate. The mixture was added into conical flasks, and then agitated on an orbital shaker at various temperatures (20, 30 and 40 °C). The experiment was conducted at various times for 8 hrs, 20 hrs, 40 hrs and 48 hrs. The pH was measured after shaking and then the samples were centrifuged for 10 minutes at 4000 rpm and the supernatant was analysed as described above.

4.3. Analytical Method

The concentration of each metal in the supernatant was analysed by using inductively-coupled plasma (ICP-OES). The mineralogical study of the tailings samples were carried out by means of X-ray diffraction (XRD) analysis. The bulk composition was determined using the powder diffraction method, after grinding and homogenization of the samples to 75 µm particle size. Non-oriented powders were examined on a Philips X'pert MPD diffractometer, at a power of 1.6 kW operating at 40KV. Major and trace elements of the tailings were analysed using the X-ray- fluorescence spectrometer (XRF) which was done on the magiX PRO SuperQ Version 4. A rhodium (Rh) anode was utilized in the X-ray tube and operated at 50 kV and current 125 mA; at power level of 4 kW.

4.4 Results

4.4.1 Characterization of mine tailings

4.4.1.1 XRD

The mineralogical composition of the representative samples used in this study is summarized in Table 1. The mineralogical composition of tailing samples from the Krugersdorp mining area was determined by X-ray diffraction (XRD). The XRD pattern showed the dominance of quartz (SiO_2) minerals on the top and bottom of the tailing dump, while other minerals, such as iron catena-silicate & ferrosilite, sillimanate, and aluminium iron (III) oxide were detected in relatively high concentration in samples. A similar trend about the dominance of quartz in the tailings was reported in the study by Novhe *et al.* (2014).

Table 1: mineralogical composition of tailing sample

Minerals	Top sample (S13) weight %	Bottom sample (S2) weight %
Quartz		85
Fayalite	3.3	
Sillimanate	0.27	8.2
Iron catena-sillicate, ferrosilite	0.6	
Wustite		6.56

4.4.1.2 XRF

The major, minor and trace elements were determined by using XRF analysis, represented in Table 2. SiO_2 is the dominant oxide in all samples collected from the Krugersdorp mining area, which is ranging from 81.37% to 89.15%. This confirms the result obtained using the XRD technique. Other studies also found SiO_2 to be mostly abundant in mine tailings (Novhe *et al.*, 2014). Elements such as Al, Cr, Ni, Zn, Cu, As, Pb, K, Mg, Na and Co were also identified in the tailings samples, but were not present in all samples. Those which were found in all samples include elements such as Ca, Cr, Fe, K, Mg, Na, Pb and Zn, however in the present study only Al and Fe remained as main focus because they were also detected when varying all other parameters considered.

Table 2: Major and trace elements in tailing samples

Samples	**Weight%**		
	Al_2O_3	**Fe_2O_3**	**SiO_2**
Top sample (S2)	13.6909	2.6767	81.3664
Bottom sample (S13)	7.9628	0.9971	89.1518

4.4.2 Batch leaching experiments

4.4.2.1 Effect of contact time

Figure 1 represents the effect of time on the leaching of metals considered in the study by using the different organic acids such as oxalic, citric, tartaric, malic and gluconic acids. The metals obtained in high concentrations are likely to be easily mobilized under environmental conditions. Fe was effectively leached using oxalic, citric and gluconic acids. However leaching with gluconic has shown a slight fluctuation in concentrations of Al and Fe from S2 and S13 respectively. The maximum leaching value of Fe from the sample S2 achieved was 510.30 mg/L after 8 hours of contact and 31.12 mg/L from S13 using oxalic acid, which decreased later as both have attained lower concentration after 2 days, reaching lower values of 40.74 mg/L and 1.38 mg/L respectively. Leaching of Fe from S2 and S13 using citric acid allowed achieving maximum release at 8 hours equivalent to 544.32 mg/L and 18.71 mg/L respectively, which decreased after some time. The leaching of Al from S2 was most effective and faster while using oxalic and citric acid, reaching maximum concentrations at 8 hours equivalent to 33.43 mg/L and 29.67

mg/L respectively. The same acids also performed better than other in extracting Al from S13 achieving a maximum release at 8 hours equivalent to 43.26 mg/l and 40.40 mg/L. It was however observed that the release of Fe and Al by tartaric acid, malic and gluconic acids fluctuates after some hours of leaching. These fluctuations of metal concentration maybe due to the reaction which take too long because of hydrolysis and precipitation of those acids (Guo *et al.*, 2013). The results have shown a decrease in Fe concentration for top and bottom sample of tailing dump with an increase in leaching time, which indicate the very high leaching rate at early stages of leaching. Overall oxalic and citric acid were very effective for the mobilization of Al and Fe from both samples as both acids exhibit high leaching rate within the early hours of contact. The higher the concentration of metals the higher is the efficiency. The achievement of higher concentration by oxalic and citric acids during early hours of leaching might be due to the fact that those acids have the ability to form stable complexes with metals that have greater potential to mobilize in the soil than those which do not (Kim *et al.*, 2013)

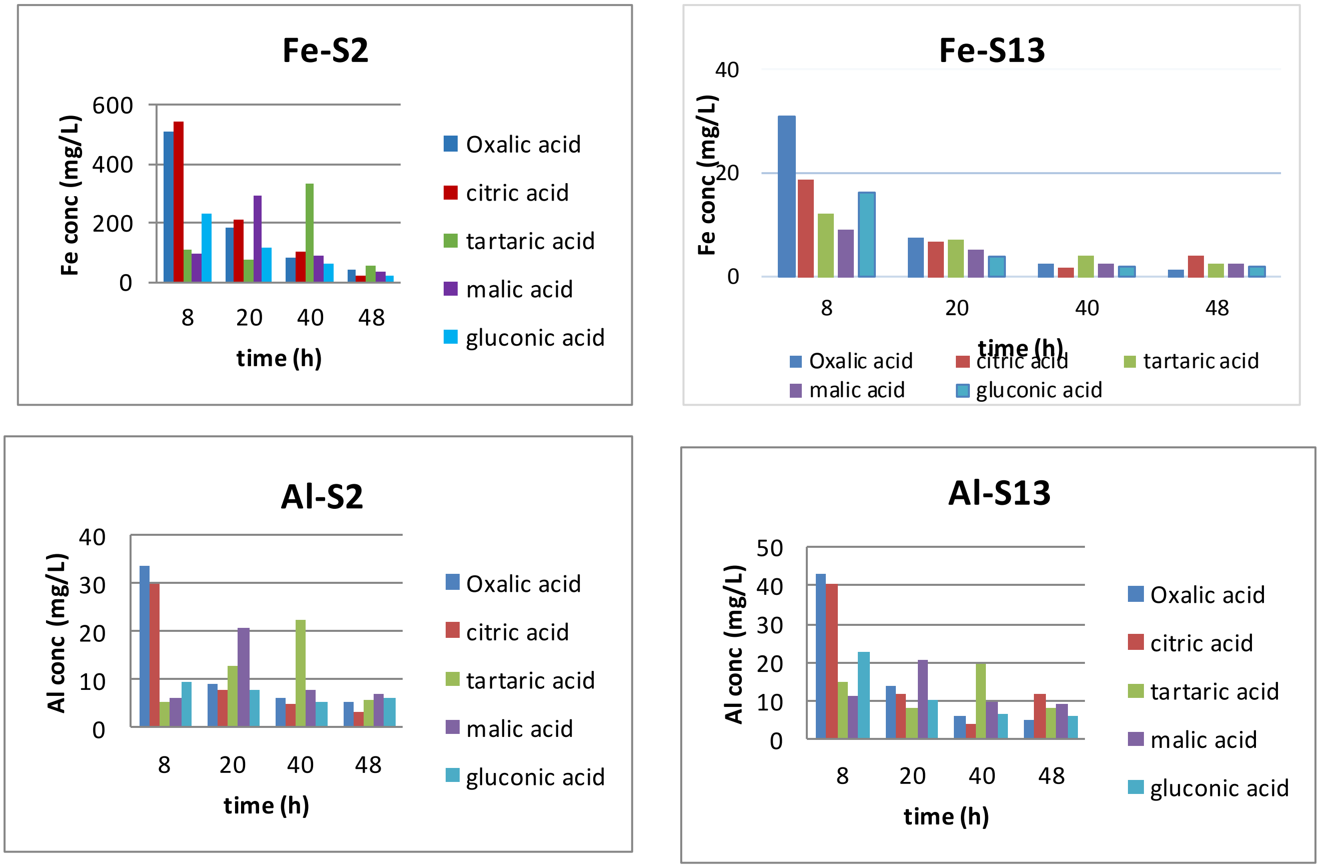
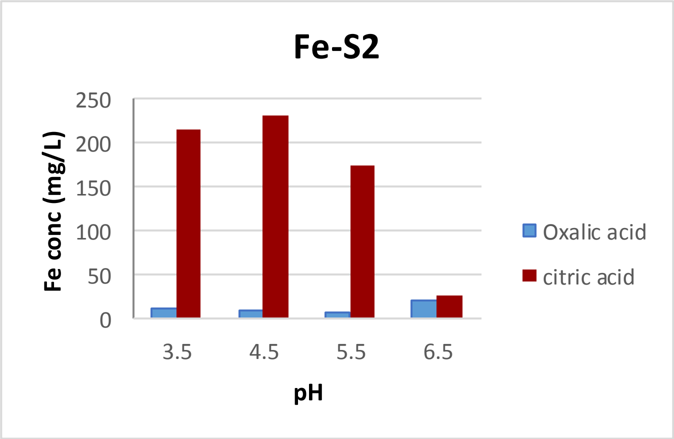
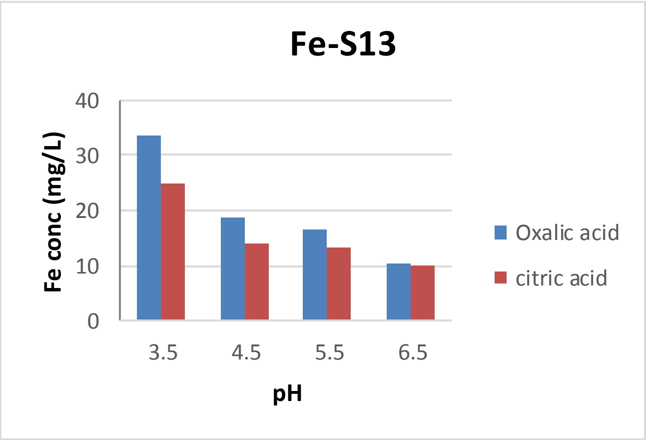


Figure1: Effect of leaching time on the extraction of Fe and Al using 3mM organic acids

4.4.2.2 Effect of pH

Figure 2 represents the results for the leaching behaviour of Fe and Al at various pHs 3.5, 4.5, 5.5 and 6.5. From the figure it is clear that the leachability profile of Al and Fe was a function of initial pH and the released amounts decrease with increasing pH value. Similar trend has been found in other studies (Fan et al., 2016; Guo *et al.*, 2013). The maximum removal of both Fe and Al appeared at pH 2. The maximum amounts of Al and Fe while leaching with oxalic acid from S2 sample are 11.92 mg/L and 11.69 mg/L respectively and the maximum amounts of Al and Fe from S13 while leaching with the same organic acid is 19.17 mg/L and 33.71 mg/L respectively. The amounts of Al and Fe leached with citric acid are as follow 24.81 mg/L and 213.77 mg/L respectively; for S2 and for S13 the amounts leached out with citric acids for S13 sample are 26.32 mg/L Al and 24.99 mg/L. Fe in the top (S2) of the tailing dump has shown high mobility than the one released from the S13 sample when citric acids was used as a leaching agent, this might be due to the fact that sample S2 is at high oxidation state compared to sample S13. The mobility of metals is high under acidic condition (low pH), according to Fan *et al.* (2016), the leaching of metals in such trend is due to the acidic attack. Al in the top and bottom samples is released in high concentration while leached with citric acid than with oxalic acid. High concentration of Fe has been released from top sample than from bottom sample, probably because of the reason already mentioned.





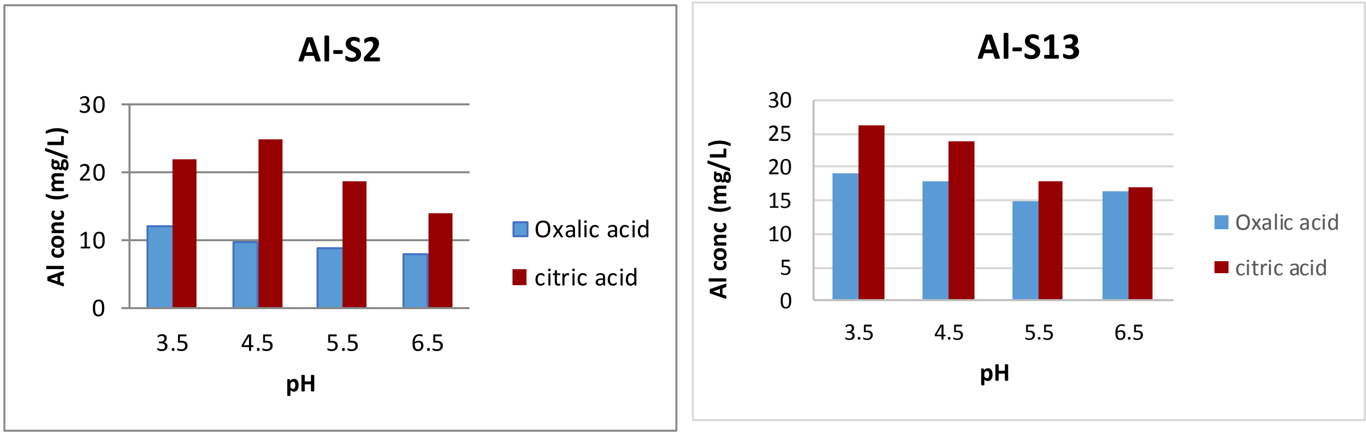


Figure 2: Effect of pH on release of Al and Fe from the top (S2) and bottom (S13) of tailing dump at 3mM oxalic acid and 48 hours contact time.

4.2.2.3. Effect of Concentration

Figure 3 illustrates the effect of organic acids concentrations on the mobility of metals at time interval 8, 20, 40 and 48 minutes. From the figure, it is evident that the mobility of metals depends on the organic acids concentrations. For both S2 and S13 samples, the concentrations of Fe and Al increase with the concentration of oxalic and citric acids from 1 mM to 4 mM. The higher the concentration of a metal, the higher its mobility. Generally high oxalic and citric acids concentrations enhance the mobilization of heavy metals from the polluted sites (Kim *et al*., 2013). The highest Al extraction from samples S2 and S13 are 25.96 mg/L and 18.86 mg/L respectively while using oxalic acid, and 17.61 mg/L and 25.96 mg/L from S2 and S13 respectively while leaching with citric acid. Fe was extracted from S2 and S13 in high amount by using 4 mM oxalic acid yielding to concentrations of 157.45 mg/L and 17.41 mg/L respectively, while 310.30 mg/L and 22.13 mg/L of Fe were the highest amounts extracted by citric acid at 4 mM from samples S2 and S13 respectively. The increasing concentration of metals at increasing concentration of acids has been established in other studies (Kim *et al*., 2013). The mobility of Fe from sample S2 was higher than from sample S13, this might be due to the fact that the oxidation at the top of tailing dump is higher than at the bottom of the tailing dump, and this has been confirmed by the XRD findings.

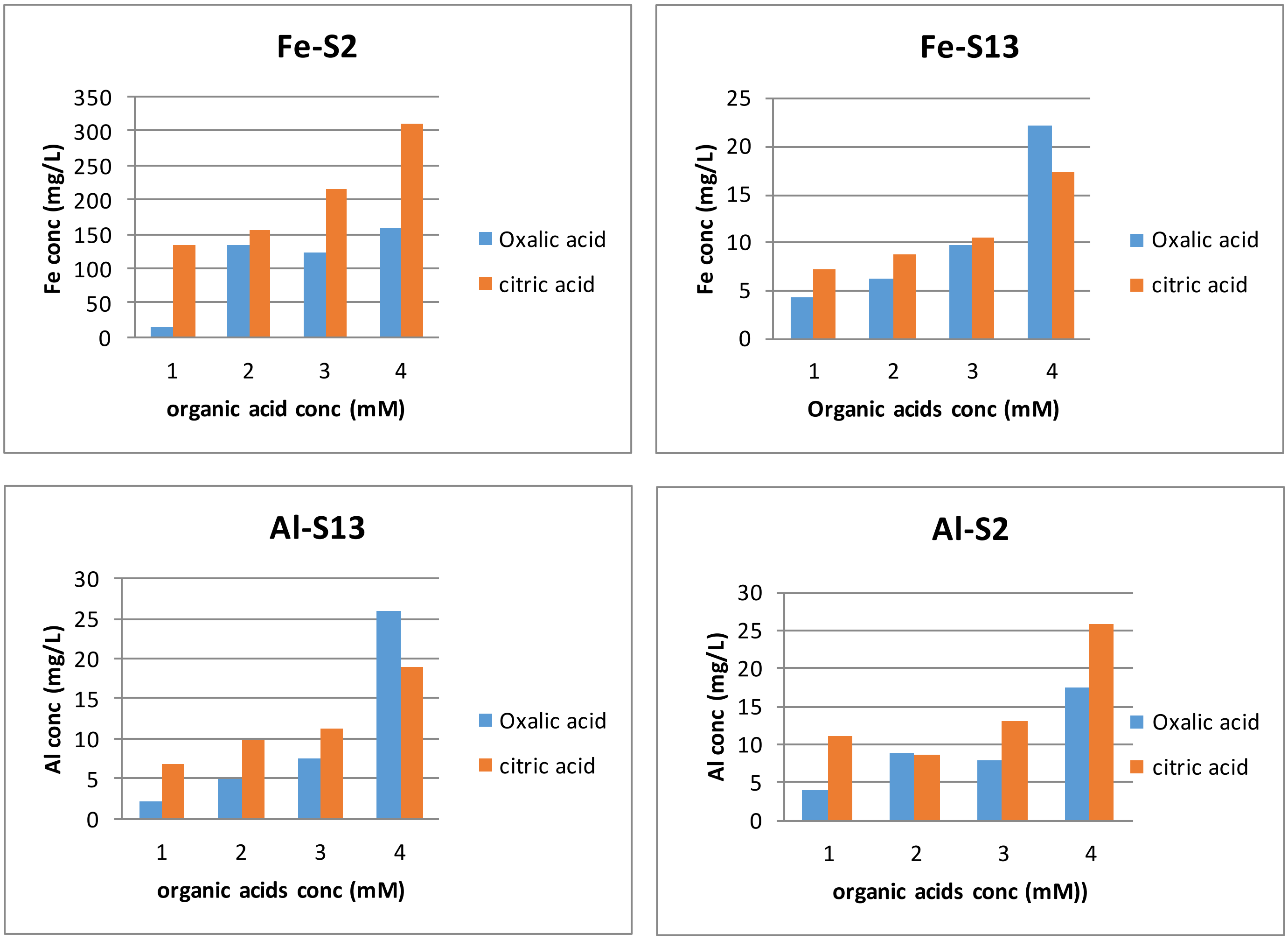


Figure 3: Effect of concentration of organic acids on the release of Al and Fe from the top (S2) and bottom (S13) of tailing dump

4.4.2.4 Effect of temperature

Figure 4 is showing the effect of temperature on the mobilization of Fe and Al when leached with oxalic acid and citric acid over temperature range from 30 to 50°C. As shown in the figure, the leaching of Al and Fe examined depend on the temperature and contact time. Leaching with oxalic acid reveals that the concentration of Fe is higher at temperature 50°C than at 30°C and 40°C. The mobility of Al and Fe increases with an increase in leaching time, which means that more time is required to mobilize higher amounts of these metals. Metals were highly removed after 48 hours with oxalic acid, as Fe from sample S2 have shown the following removal pattern 0.89 mg/L at 30°C, 0.98 mg/L at 40°C and 1.36 mg/L at 50°C. Whereas Al from S2 has shown the following releasing pattern at 48 hours; 0.30 mg/L. at 30°C, 0.41 mg/L at 40°C and 0.44 mg/L at 50°C when leached out by oxalic acids. The same metals show the same leaching behaviour for sample S2 when oxalic acid is used, and when both metals from S2 and S13 are leached with citric acid. The trend where by metals are removed in higher concentration at higher temperature than at low temperature has been reported in other studies (Guo *et al.*, 2013; Habache *et al.*, 2009).

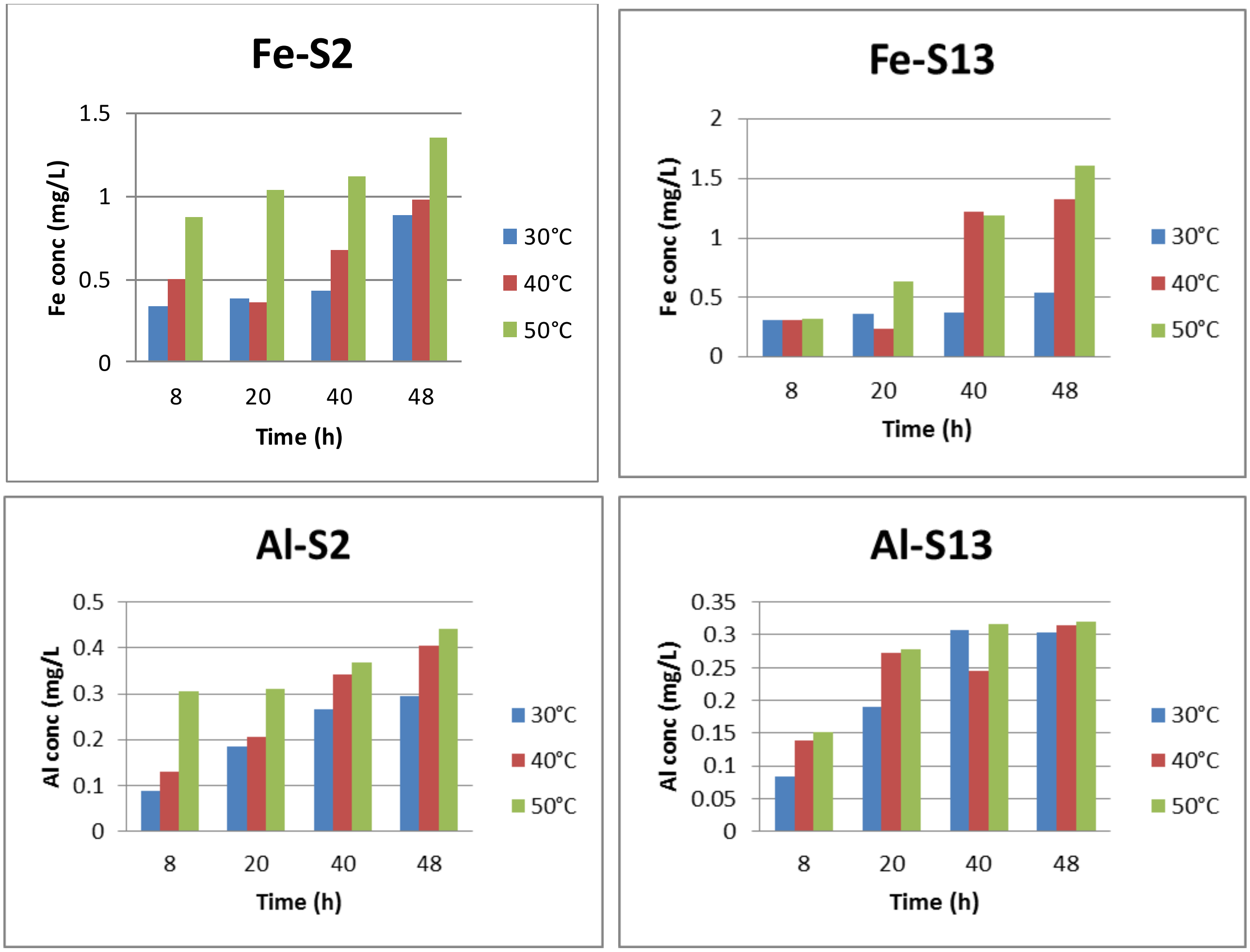


Figure 4.1: Effect of temperature on the release of Al and Fe from the top (S2) and bottom (S13) of tailing dump at 3mM oxalic

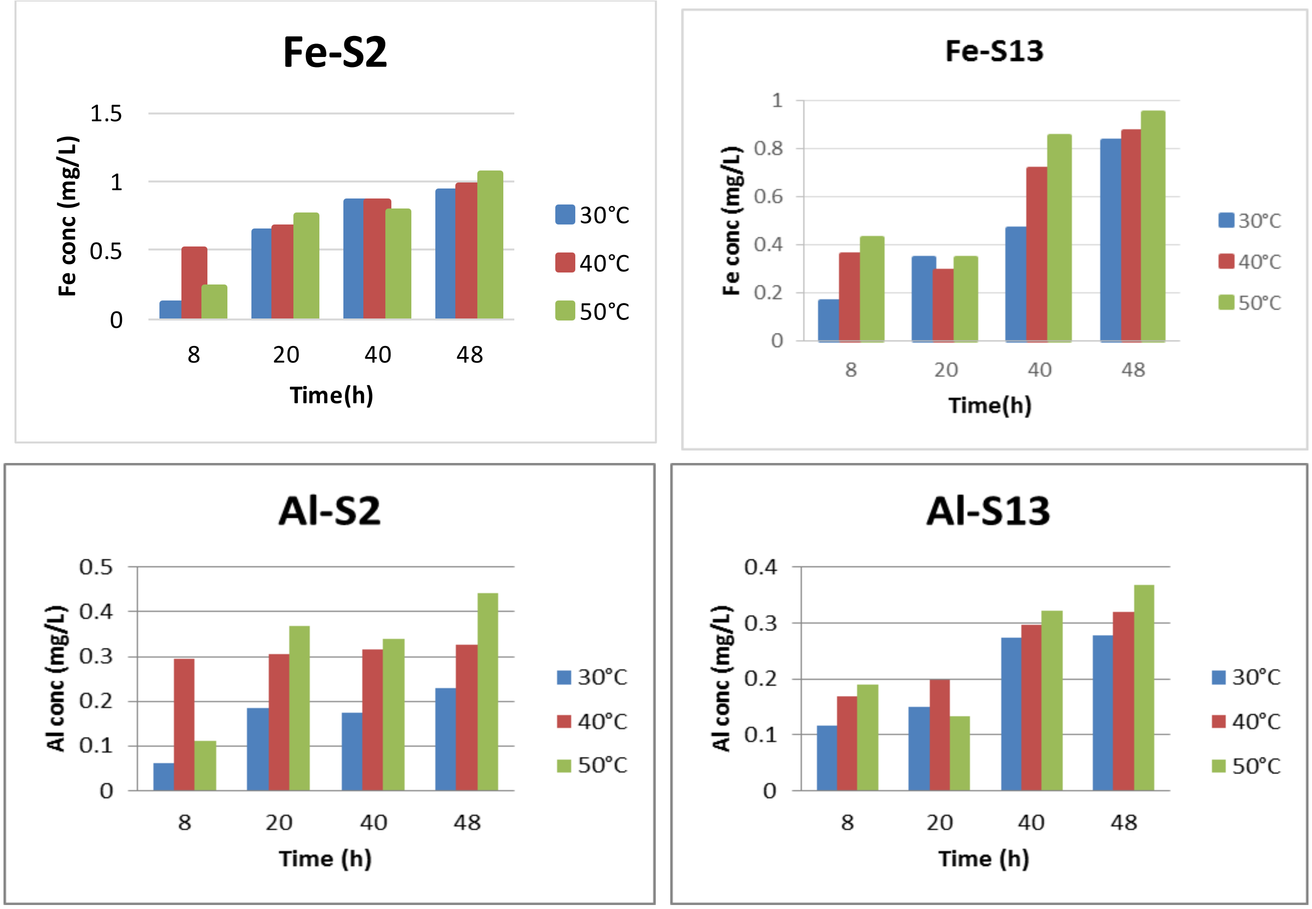


Figure 4.2: Effect of temperature on the release of Al and Fe from the top (S2) and bottom (S13) of tailing dump at 3mM citric acid during 48 hours of contact time

4.2.2.5 Effect of temperature – Synergy of organic acids

Table 3 exhibits the effect of the combination of organic acids (oxalic, citric, tartaric, malic and gluconic) on the mobility of metals in various contact time of 8, 20, 40 and 48 hours. The results show that the concentration of Fe decreases with leaching time, which illustrates that when this organic acids are combined together, they are more effective in leaching the metals at the initial leaching time than when each organic acid is used. At initial hours of leaching the mobility of metals is high for sample S2, when leaching with organic acids in synergy. The concentration of Fe decreases from 1.5 mg/L to 0.56 mg/L from 8 to 20 hours at 30°C , at 40°C it decreases from 2.09 mg/L to 0.67 mg/L and in S13, the decrease from 8 to 20 hours at 30°C is 3.09 mg/L to 1.86 mg/L and remained undetected at 40 and 48 hours. The increase in leaching time from 8, 40 and 48 hours at 40°C has shown the attenuation of amounts released from 3.29 mg/L, 1.20 mg/L to 1.47 mg/L. Al was released in high amount from sample S2 at 8 hours and temperatures of 30°C, 40°C and 50°C, yielding to concentrations equivalent to 12.48 mg/L, 20.42 mg/L and 22.09 mg/L respectively, which further decrease after 48 hours to the following concentrations 4.92 mg/L, 5.49 mg/L and 8.80 mg/L. The maximum amount of Al was leached at 8 hours at temperatures of 30°C, 40°C and 50°C, yielding concentrations equivalent to 21.01 mg/L, 25.22 mg/L and 25.97 mg/L, then a decrease was recorded in the following hours to 6.29 mg/L, 6.35 mg/L and 7.88 mg/L respectively. Fe from samples S2 and S13 exhibit similar trend than Al, however in some cases Fe is not detected. The synergy of all organic acids, allows mobilizing more metals in the first hours of leaching time under the influence of temperature; this is favourable for high leaching rate.

Table3: Effect of synergic action of organic acids on the leaching of Al and Fe

Elements	**Temperature**	**Amounts removed per leaching time (mg/L)**			
		8	**20**	**40**	**48**
Fe (S2)	30°C	1.539	0.558	0.000	0.000
	40°C	2.086	0.666	0.000	0.000
	50°C	0.000	2.182	1.781	0.494
Fe (S13)	30°C	3.086	1.862	0.000	0.000
	40°C	3.287	0.000	1.197	1.465
	50°C	0.000	3.164	1.001	0.000
Al (S2)	30°C	12.476	7.405	7.218	4.921
	40°C	20.424	8.136	7.538	5.488
	50°C	22.093	8.443	9.497	8.796
Al (S13)	30°C	21.009	11.845	8.635	6.288
	40°C	25.215	14.593	10.681	6.355
	50°C	25.970	18.229	3.913	7.881

4.4.2.6 Kinetic studies

Leaching kinetics is generally controlled either by diffusional mass transfer reactant through a liquid film or ash/product layer, the chemical reaction or a mixture of diffusion and chemical reactions (Gharabaghi et al., 2013; Sahu et al., 2011; Gharabaghi et al., 2010, Levenspiel, 1998, Zafari, 2008). The reaction model between the interaction of liquid and solid may be expressed as:

$$A(liquid) + B(Solid) \rightarrow products \qquad (1)$$

In order to determine the kinetic parameters and the rate controlling step in the Iron and Aluminum leaching in oxalic acid solutions, the experimental data were analysed based on the shrinking core model. The following equations can be used when either diffusion or the surface chemical reactions are the rate limiting step.

$$x = kt \qquad for\ liquid\ film\ diffusion \qquad (2)$$

$$1 - 3(1-x)^{\frac{2}{3}} + 2(1-x) = kt \qquad for\ film\ diffusion\ control\ through\ ash\ layer \qquad (3)$$

$$1 - (1-x)^{\frac{1}{3}} = kt \qquad for\ surface\ chemical\ reaction\ control \qquad (4)$$

Where x is the fraction reaction reacted, k is the kinetic constant (min^{-1}/h^{-1}).

The rate limiting step is determined by looking at the high regression coefficients (R close to 1), which reveal a better fitting plot as shown in Figures 5.1 and 5.2. When the regression coefficients for kinetics controlled by different regimes were calculated, as shown in Tables 5.1 and 5.2 the highest regression coefficient or the best fits for all the experimental results for tailing leaching using organic acids were found for rate expression controlled by diffusion through ash layer, but the fit was dependent of particle shape which varied among the two samples. Using oxalic acid as lixiviant, a better fit was mostly obtained when assuming particle of flat shape; it could be predicted that the dissolution of Fe was mostly controlled by ash layer diffusion when leaching took place at 30°C; while the dissolution of Al was controlled by film diffusion in S2 and ash layer diffusion in S13.

The fit of the experimental data for the leaching of tailing by citric acid revealed that Fe dissolution from S2 was better controlled by ash layer diffusion with assumption of spherical particle, while the dissolution from S13 was better controlled by ash layer diffusion but with assumption of flat particle. On the other hand, dissolution of Al revealed an inverse trend to that of Fe; as it was found to be controlled by ash layer diffusion with assumption of flat particle in S2, but in S13 the particle was spherical. The different leaching patterns obtained while using oxalic and citric acids in this study is not only linked to the nature of the organic acids as found by Sahu *et al.* (2011), but the physico and geochemical difference among the samples might have had an impact. For the sample from the top (S2) and the bottom (S13) in terms of the rate limiting step, this implies that the release is based on the geochemical particles confirmed by the results of the XRF. The rate constant K was evaluated from the slope of the straight lines shown in Figures5. Arrhenius equation K =A$e(^{-Ea/RT})$ was plotted as lnK vs (1/T) and Ea were calculated. The activation energies determined were found to be mostly lower than 80, confirming that the metal dissolution rate is predominantly diffusion controlled (Habashi, 1999; Aydogan *et al.*, 2005).

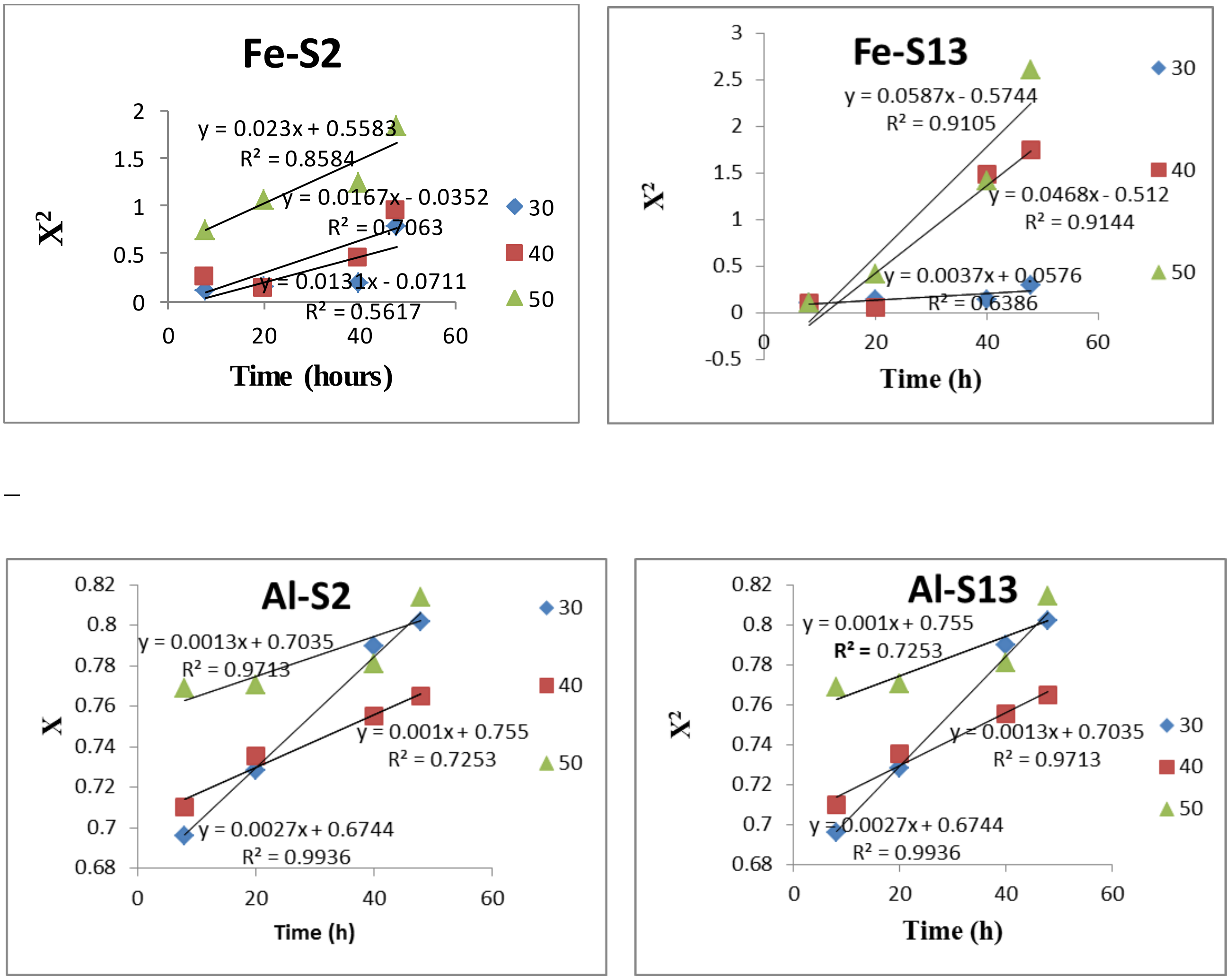


Figure 5.1: Plots of x vs. leaching time at different temperatures for the dissolution of Al and Fe from top (S2) and bottom (S13) of tailing dump with oxalic acid solutions

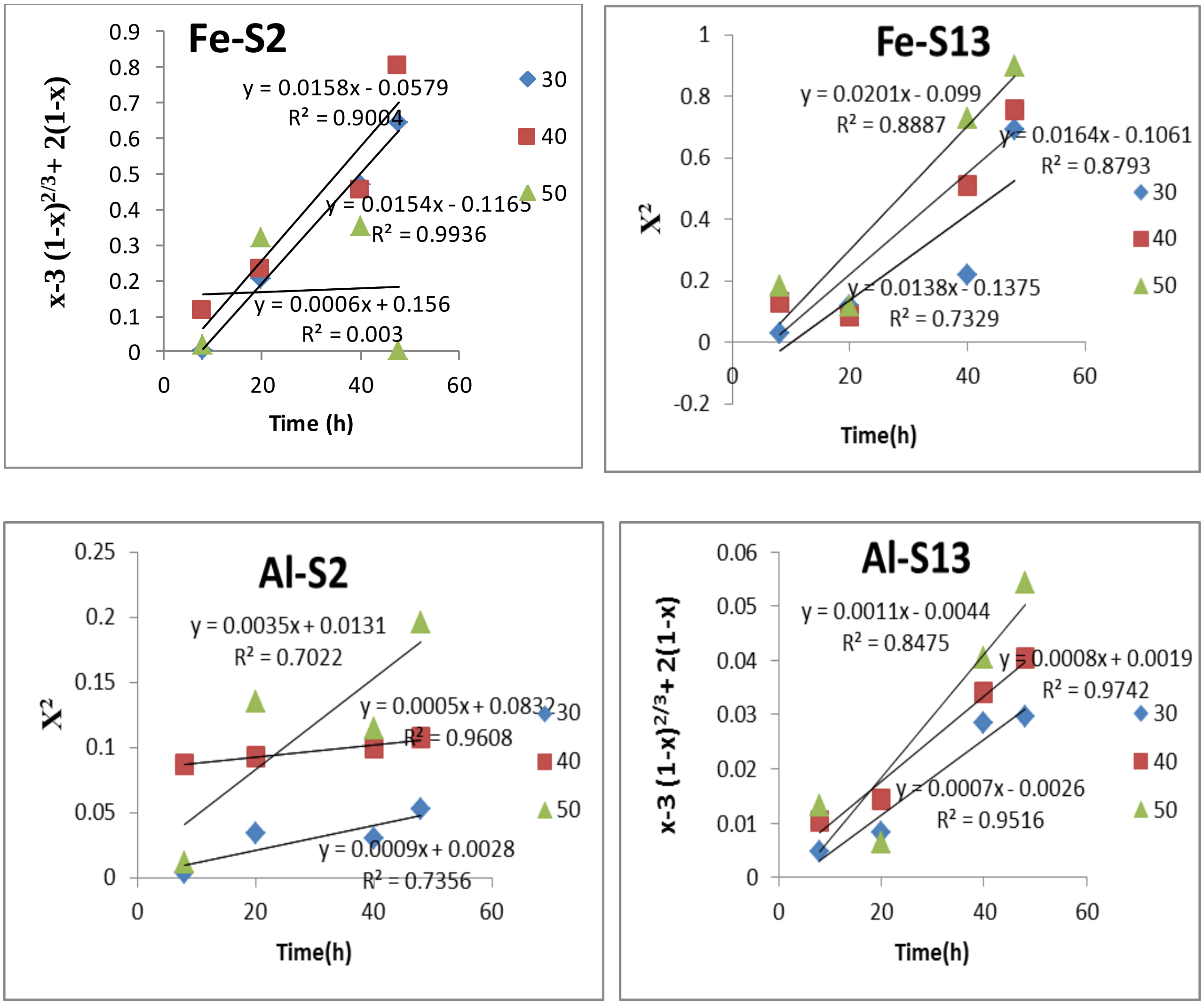


Figure 5.2: Plots of x vs. leaching time at different temperatures for the dissolution of Al and Fe from top (S2) and bottom (S13) of tailing dump with citric acid solutions

Table 5.1: Kinetics equations and their regression coefficient and activation energies when using oxalic acids as lixiviant

metals	**Kinetic equation**	**slope**	**R**	**Ea**
Fe- top	Y=-2.7559X+4.7401	-2.7559	0.9889	22.91296
Fe-bottom	Y=-13.699X+39.941	-13.699	0.8251	113.8925
Al-top	Y=5.055X-21.542	5.055	0.9479	42.0271
Al-bottom	Y=1.8742X-11.468	1.8742	0.4852	15.5825

Table5.2: Kinetics equations and their regression coefficient and activation energies when using citric acid as lixiviant

metals	**Kinetic equation**	**slope**	**R**	**Ea**
Fe- top	Y=-20.229+61.868	-20.229	0.7387	2.084651
Fe-bottom	Y=-1.8X+1.6992	-1.8145	0.9962	15.08584
Al-top	Y=-0.1021X+3.3997	-0.102	0.9997	52.14982
Al-bottom	Y=-2.3765X +0.531	-2.3765	0.9145	9.72893

4.5. Conclusion

It was found that the mobility of Al and Fe elements were highly influenced by environmental conditions. Citric and oxalic acids were found to be the most efficient leaching agents as both yielded fast dissolution rate of metals from both tailing samples. Fe and Al were mobilized efficiently in high acidic medium and high temperature conditions. It was also observed that when acting in synergy, organic acids were more efficient as lixiviant than when considered individually; this could be ascribed to the diversity of leaching mechanisms. The kinetic studies allowed determining the rate limiting steps for the dissolution of metals which is critical for the improvement of the leaching rate; most of the rate expressions were diffusion controlled, implying that the physical properties of the tailing significantly influenced the leaching rate.

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References

Aydogan, S., Ucar, G. & Canbazoglu, M. 2005. Dissolution kinetics of chalcopyrite in acidic potassium dichromate solution. *Hydrometallurgy*, 81(2006), 45-51.

Brandl1 H and Faramarzi M.A, (2006). Microbe-metal-interactions for the biotechnological treatment of metal-containing solid waste.*China Particuology*. 4, 93-97.

Ding Y.Z • Song Z.G • Feng R.W • Guo, J. K. 2014. Interaction of organic acids and pH on multi-heavy metal extraction from alkaline and acid mine soils. *Int. J. Environ. Sci. Technol*. 11, 33-42.

Gadd G.M, (2004). Microbial influence on metal mobility and application for bioremediation. *Geoderma* .122, 109– 119.

Gharabaghi M, Irannajad M, Azadmehi A.R, *2013*. Leaching kinetics of nickel extraction from hazardous waste by sulphuric acid and optimization dissolution conditions. *Chemical Engineering Research and Design* 9, 1, 325–331.

Kundu S, Rathore A.S, Pushp A and Chundawat V.S, 2014. Batch Investigations on Elemental Dissolution from Copper Mine Tailing Pond, Khetri, India: Evaluation of the Environmental. Contamination Potential International Conference on Chemical, *Civil and Environmental Engineering*. 18-19.

Fan L, Zhou X, Luo H, Deng J, Dai L, Ju Z, Zhu Z, Zou L, Ji L, Li B and Cheng L, 2016. Release of Heavy Metals from the Pyrite Tailings of Huangjiagou Pyrite Mine: Batch Experiments.*Sustainability*. 8, 96.

Guo Y, Huang P, ZhangW, Yuan X, Fan F,Wang H, Liu J,Wang Z, 2013. Leaching of heavy metals from Dexing copper mine tailings pond. Trans. *Nonferrous Met. Soc*. 23, 3068−3075.

Habashi, F., 1999. Kinetics of Metallurgical Processes, 2nd ed. *Metallurgies Extractive Quebec, Quebec*, Canada.

Habbache N, Alane N, Djerad S, Tifouti L, 2009. Leaching of copper oxide with different acid solutions. Chemical Engineering Journa*l. 152, 503-508***.**

Kim J, Lee Y and Chung J, 2013. The Role of Organic Acids in the Mobilization of Heavy Metals from Soil. *KSCE Journal of Civil Engineering* (2013) 17(7), 1596-1602

Mishra D, Kim D, Ahn J and Rhee Y, 2005. Bioleaching: A Microbial Process of Metal Recovery; A Review. *Metals and materials International*. 11, 249-256.

Misra V, Tiwari A, Shukla B, Seth C.S, 2009. Effects of soil amendments on the bioavailability of heavy metals from zinc mine tailings. Environ Monit Assess. 155, 467–475.

Novhe N.O, Yibas B, Netshitungulwana R and Lusunzi R, 2014. Geochemical and mineralogical characterization of mine residue deposits in the Komati/Crocodile catchment, South Africa: an assessment for acid/alkaline mine drainage *ISBN*. 978-7-5646-2437-8.

Oelefse S.H.H, Hobbs P.J, Rascher J and Cobbing J.E, 2007. The pollution and destruction threat of gold mining waste on the Witwatersrand - A West Rand case study.

Wuana R. A, Okieimen F. E, Imborvungu J. A, 2010. Removal of heavy metals from a contaminated soil using organic chelating acids. *Int. J. Environ. Sci. Tech*., 7 (3), 485-496, ISSN: 1735-1472.

Sayer and Gadd, 2001. Binding of cobalt and zinc by organic acids and culture filtrates of *Aspergillus niger* grown in the absence or presence of insoluble cobalt or zinc phosphate.105 (10), 1261-126.

CHAPTER 5

Article 3

Introduction

This paper addresses column leaching of tailings dumps from gold mines in South Africa.

The following objectives were reached:

To evaluate the pH, EC, major anion and redox potential and also to predict the potential of acid regeneration.

The research findings showed that the gold mine tailings evaluated have the potential to generate acid, as neutralization potential is less than the acid generation potential. It was also found that addition of compost more effectively decreased the mobility of heavy metals. Addition of compost also increases the pH of the leachate, increasing the alkalinity. High concentrations of sulphate were found due to oxidation of sulphides, which is likely to cause AMD. The PHREEQC results revealed that the free hydrated metal ions dominated the complexed metals, which is likely to cause high toxicity in receiving waters.

Column leaching of tailings dumps from gold mine in South Africa and implication of organic matters.

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Abstract

Untreated abandoned mine tailings may results in hazards to the environment due to toxic elements. Column experiments of 15 weeks duration evaluated the leaching of Cu, Ni and Zn in mine tailings treated with compost. One sample was not treated. Parameters such as pH, electrical conductivity (EC), redox potential (E_h), Cl^-, SO_4^{2-} and alkalinity were assessed. Acid-base accounting (ABA) was conducted in order to predict the balance between the acid released and neutrality. XRD (X-ray diffraction) was also employed in order to determine the mineralogical composition. The speciation of metals in the leachate was modelled using the PHREEQC. The results showed that quartz minerals were abundant in the tailings, and other minerals include pyrophylite, hautrurite, andulusite, brown millerite and calcium iron (III) oxide. The Cu, Zn and Ni mobility was decreased by the addition of compost. The tailings samples were found to have potential to generate acid. The tailings were also found to lack alkalinity in most sampling areas, as they had a pH of less than 4. The high acid mine tailings are likely to mobilize metals effectively and pollute the ecosystem. The speciation concentrations point towards domination by the free hydrated ions in the mine tailings, which facilitate distribution and cause toxicity in the surface.

***Keywords*:** mine tailings, compost, toxicity, metal speciation, metal mobility

5.1Introduction

South Africa is a mineral-rich country with metals such as gold, copper, and the platinum group metals having been utilized to a significant extent in the country's mining history (Malatse and Ndlovu, 2015). Mining of these valuable metals generate the solid wastes which are divided into two categories: wastes rock and mine tailings (Johnson 2014). Gold mining was reported to be the largest source of pollution as it accounts the highest percentage of all minerals produced in the country (Oelofse, 2008; DWAF, 2001).

Mine tailings are the wastes generated by the mining industry, and are regarded as the main source of environmental contamination, as opposed to waste rock and other waste materials (Bampah *et al.*, 2013). The disposal of mine wastes (waste rock dumps, tailings and slags) without any environmental care, may cause greater soil contamination (Andre´s andFrancisco, 2008). Oxidation of sulphide minerals results in acid mine drainage (AMD), which is able to degrade streams due to its low pH and consequent mobilization of metals (Jia *et al.*, 2014). The oxygenation process happens when oxygenated rainwater combines with mine tailings (Grover *et al.*, 2016: Stumm and Morgan, 1996). AMD from the pyrite oxidation may take place if the acid potential (AP) is higher than the neutralization potential (NP) (Kaartinen and Wahlstrom, 2009). Mine tailings cause more problems if it is not covered, as it is then able to degrade and migrate to the bottom of the dump and neighbouring areas (Liefferink, 2011).. The abandoned mine tailings dump in the Krugersdorp mining area has been eroded and moved to the bottom of the dump, together with metals, and is the reason why most rivers nearby are acidic. In this regard Du Toit (2010) has established that,in 2002, near the town of Krugersdorp, AMD also welled up and began pouring out on the surface. Since then about 15 million litres a day of AMD have been spilling out. The mobility of heavy metals in mine tailings is controlled by a range of physical and chemical factors, such as pH, redox potential, mineral and chemical compositions, and grain size (Kim, 2014). Management of the mine tailings problem is regarded as a serious challenge to the mining industry worldwide (Jia *et al.*, 2014). There are a couple of methods which were implemented to manage the tailings problem. Mine tailings have been successfully re-vegetated through the application of highly organic matter amendments such as municipal biosolids and composts in combination with limestone or high calcium carbonate equivalent residuals (Brown *et al.*, 2007; Brown *et al.*, 2003, Brown *et al.*, 2005aandDeVolder *et al.*, 2003). Other studies have established that the remediation of metal-contaminated sites is possible by means of a variety of acid neutralization and metal removal treatments based on the use of alkaline materials such as limestone (Flores and Sola, 2010; Cravotta and Watzlaf 2002; Nicholson *et al.* 1988, 1990; Younger *et al.* 2002).

Hence it is imperative to study the mobility of these metals while the metals are composted and when not composted, in order to find a way of managing the mine tailings problem. The column and batch leaching experiments are the most used processes in assessing the mobility of elements in the mine tailings (Kundu *et al.*, 2014). Column methods predict exactly the situation occurring in the field, which is not possible with the batch leaching method. According to Lackovic (1997), although column leaching is more expensive than batch leaching, it predicts the potential mobility, as the column leaching represents the prevailing environmental conditions. The objective of this study is to evaluate the pH, EC, major anion and redox potential and also to predict the potential for acid generation.

5.2 Methodology

5.2.1 Materials

Mine tailings (0-30 cm depth) were sampled from the abandoned gold mine tailings dump in the Krugersdorp area, South Africa. Three representative samples from the top, middle and bottom of the tailings dump were collected. Compost purchased from Garden Pavilion in Potchefstroom was used as the organic amendment of the tailings. Mine tailings were mixed together to form a complex sample and kept in plastic bags before use.

5.2.2. Characterization of mine tailings

Mine tailings were characterized through the determination of its mineralogical composition, chemical analysis and also the particle size distribution. The mineralogical investigation of the tailings samples were conducted by means of X-ray diffraction (XRD) analysis. The bulk composition was evaluated using the powder diffraction method, after Crushing and homogenization of the samples to 75 µm particle sizes. Non-oriented powders were examined on a Philips X'pert MPD diffractometer, at a power of 1.6 kW operating at 40KV. The particle distribution for the representative sample from the top (sample 1), middle (sample 2) and bottom (sample 3) of tailings is shown in Figure 2 and was determined using the Malvern, performance verification, UK.

5.2.3. Column leaching

Twelve identical columns were set up to carry out column tests, as shown in Figure 1. The setup consisted of three columns with samples from the top, middle and bottom of the tailings dump, and which contained tailings plus compost (experimental) and 3 control columns which contained only tailings. The controls and the experiments were all carried out in duplicate. 600 g of tailings and 120 g of compost were mixed together before packing in the columns, with the control columns receiving only 600 g of tailings. For all the columns water was added up to 10 cm from the top of the packed materials. Leachates were collected continuously from the bottom of each column after a cycle of one week for 15 weeks. After each collection the metal analyses were conducted, using an inductively coupled plasma optical emission spectrometer (ICP-OES). After each collection of samples, pH, temperature, electric conductivity (EC) and redox potential were measured. Such parameters were measured by using a probe integrated to pH meter (Hanna Instruments Inc., USA). EC was measured by using a conductivity meter with an electrode. The pH was measured after calibration with buffers. Redox potential was measured by using a pH meter with an analytical electrode. Measured values were converted to E_h. The concentration of sulphate ion (SO_4^{2-}) was measured using a COD and Multiparameter Bench Photometer HI 83099 (Hanna Instruments Inc., USA). The chloride ion test was conducted by titrating the samples with silver nitrate and 1 mL of potassium dichromate. The experiments were carried out under anaerobic conditions.

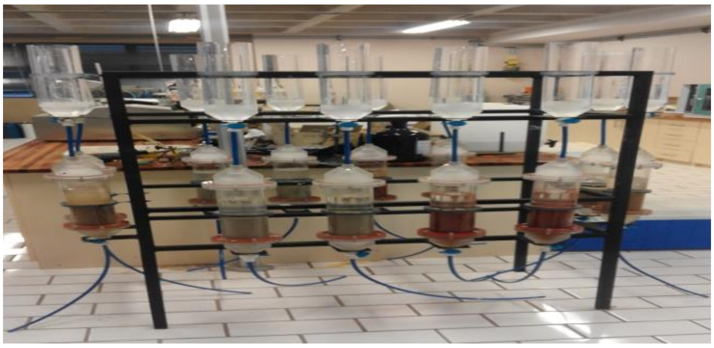


Figure 1: Column experiment setup

5 2.4. Acid base accounting

The acid base accounting which is the balance between the AP and the NP is calculated using a modified method by Lawrence and Wang, 1997. *25%* HCl were added in dropwise to 2 g of powdered tailings sample on aluminium foil. The rate of fizz was assigned as in in Table 1. 2.00 g of tailings sample was added to 90 mL of water. At the start of the test the volume of HCl according to Table 1 was added, directed by fizz rating.

Table 1: Volume of HCl Added for Various Fizz Ratings, the Modified Acid Base Accounting Procedure for Neutralization Potential (Lawrence) (from Lawrence and Wang,

Fizz Rating	Volume of 1.0 M HCl (mL)	
	At time = 0 hour	At time = 2 hour
None	1.0	1.0
Slight	2.0	1.0
Moderate	2.0	2.0
Strong	3.0	2.0

The mixture was agitated at room temperature using reciprocal shaker. After 2 hours the acid was added as in the Table 1. After 22 hours, the pH was monitored. The pH was maintained in order to remain in the range between 1.5 and 2.0. When it was greater than 2.0, a measured volume of 1.0 M HCl was added to bring the pH into the range 1.5 to 2.0. When the pH was less than 1.5, it indicated that too much acid had been added in steps 2 and 3. In this case, the test was repeated, adding a reduced volume of HCl.

After 24 hours, the test was terminated and distilled water was added to the flask to bring the volume to approximately 125 mL. The pH measured and recorded, making sure it was in the required range of 1.5 to 2.0.

The contents of the flask were titrated to a pH of 8.3 using certified or standardized 0.5N or 0.1 N NaOH.

The NP of the sample was calculated as follows:

Modified NP (kg $CaCO_3$/t)

= [(N x vol (ml) of HCl) – (N x vol (ml) NaOH) x 50] / [weight of sample (g)]

The acid potential

The potential of mine tailing sample to generate acid was calculated based on the Sulphur and sulphide content. The formula to calculate the acid potential is as follows:

AP (kg CaCO3/t) = %S= x 31.25.

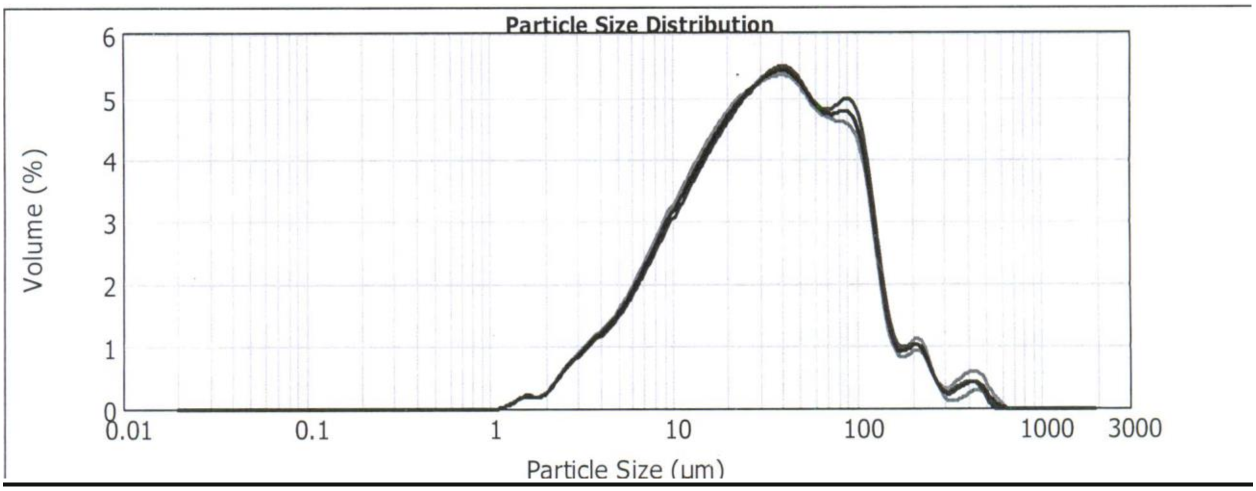
Where S= (sulphide-sulphur) = total sulphur - sulphate Sulphur

5.3. Results and discussion

5.3.1. Particle size distribution

The particle size distribution outcomes are indicated in Figures 1, 2 and 3. The results reveal that the particle sizes from the top (S1) and bottom (S3) of the tailings dump samples fall in the range between 1 and 1 000 µm. The particle sizes of the middle of the tailings dump (S2) fall in the range between 1 and 100 µm. According to Jopony *et al.*, 1987 the smaller particles have a large surface area and thus likely to liberate metals in high concentrations. It is therefore likely that metals will be easily leached from S2 than from samples S1 and S3.

(i)



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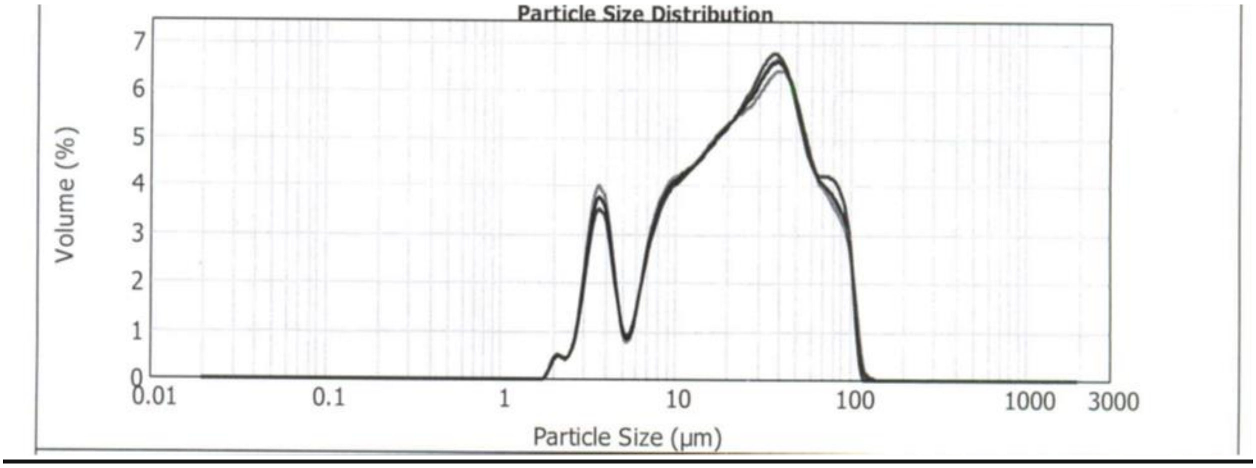

(iii)

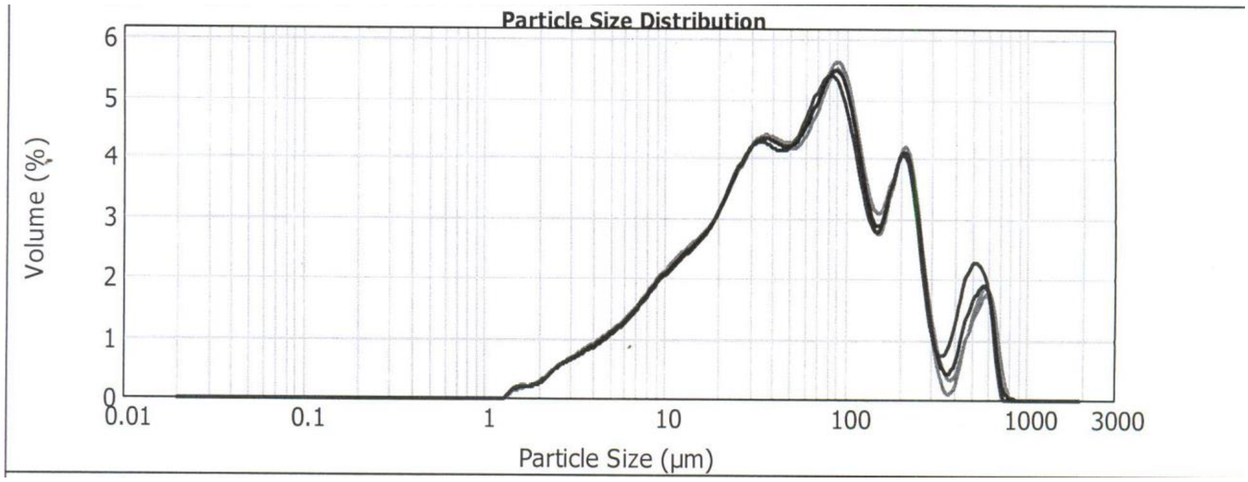

Figure 2: Particle size distribution for sample from the top (i), middle (ii) and bottom of thetailing dump (iii).

5.3.2. Mineralogical composition of mine tailings

The X-Ray diffraction (XRD) analyses of the mine tailings from the top (S1), middle (S2) and bottom (S3) of the tailings dump are shown in Table 2. The results of the mineralogical composition of the tailings show a dominance of quartz compared to other minerals, it constitutes 85% of the top samples and 91% of the bottom samples. Aluminium iron (III) oxide dominated the middle of tailings dump (60%). The mine tailings also contained pyrophylite, hautrurite, andalusite, brown millerite and calcium iron (III) oxide. Other authors also found a dominance of quartz in tailings than the other minerals (Lee, 2006; Novhe *et al.*, 2014). Samples from the middle of tailing dump exhibited high oxide minerals than sulphide minerals.

Table 2: Mineralogical composition of mine tailings

Minerals	**Weight % in each sample**		
	Top (S1)	**Middle (S2)**	**Bottom (S3)**
Quartz	84.8	9.9	91
pyrophylite1A dehydroxylate	13.5	-	8.2
Hatrurite, syn	1.6	-	-
iron(III) oxide, alpha-Fe_2O_3	4.8	-	-
Calcium Iron Oxide	-	17.8	-
Brown millerite, syn	-	-	0.98
Wollastonite-1A, ferroan	-	-	-
Andalusite	-	7.7	-
aluminium iron(III) oxide	-	60	-

5.3.3. Acid base accounting results

Table 2 shows the results of acid-base accounting, the subdivision observed is based on acid potential (AP) and the neutral potential (NP) of the mine tailings samples at the top, middle and bottom of the tailings dump. The net neutralization potential (NNP), which is the difference between the NP and AP and also the neutral potential ratio (NPR), which is the ratio between NP and AP, is calculated. Tailings samples from all sampling sites have a potential for acid generation due to the negative NNP and the NPR. Worshner *et al.* (1995), also found the negative NNP which shows the potential for acid generation.

Table 3:Acid base accounting results

Sample Name	**Fizz rating**	**NP**	**AP**	**%S**	**NNP**	**NPR**
Top (S1)	Slight	-260.5	57.57	1.842	-318.07	-4.52
Middle (S2)	Slight	-365	118.28	3.785	-481.28	-3.07
Bottom (S3)	Slight	-270	37.4	1.197	-307.4	-8.22

5.3.4. Column leaching test

The results of the column test is shown in Figure 3, which contains the concentrations of released Cu, Ni and Zn, pH measured and sulphate concentration determined during 15 weeks of leaching. Adding compost to the tailings resulted in a higher pH value in the leachate of the samples from the top (ES1A and

ES1B) and bottom (ES3A and ES3B) of the tailings dump. However, for the middle of the tailings dump (ES2A and ES2B), the pH values decreased, even after the addition of compost. The tailings without compost (CS1A, CS1B, CSB2A, CS2B, CS3A, and CS3B) all had a low pH, which ranged between 2 and 3. The increase of pH in sample containing compost was also reported by Fosberg *et al.* (2008). The pH was almost constant for each sample as only a slight variation was recorded during the leaching. The concentrations of sulphate are shown in Figure 3. The untreated tailings samples from S1 and S3 released almost equal concentration of sulphate as shown in the figure. The high acidic (low pH) samples exhibited higher concentrations of sulphate than the samples with high pH. The samples from S2 were not affected by compost treatment as it revealed high sulphate concentration, but less than that of the untreated samples from the same sampling site. The untreated sample had a maximum concentration of 14345 mg/L, which decreased in the last week of leaching to 13590 mg/L. The concentration of sulphate in treated samples from the same sampling site showed an increasing trend from 8585 mg/L to 9595 mg/L for ES2A and from 5 555mg/l to 8 585 mg/L for ES2B. The composted and non-composted samples from S1 and S3 did not show an effect on the concentration of sulphate, similar concentrations ranging from 1 530 mg/L to 3 030 mg/L were observed. The treated samples from S1 and S3 were the only ones with alkalinity, as they had pH values between 7 and 8, and the rest did not have any alkalinity, with pH values under 4.

The mobility of Cu, Ni and Zn were also assessed, as shown in Figure 3. It can be observed that the mobility of Ni and Zn is high in samples which were not treated with compost than in those which were composted. Only in ES2A and ES2B was the mobility of Cu higher than in the other columns which were leaching almost similar concentrations of other metals. The samples which released metals in high concentrations show the variability during the leaching. The concentration of metals seems to decrease from weeks 3 to 6 and from weeks 8 to 11, the concentrations tend to increase from weeks 0 to 3, weeks 6 to 8 and weeks 11 to 14. The concentration of metals tends to fluctuate from weeks 13 to 14, and from weeks 14 to 15 there was no increase. The high mobility of the samples in the control samples (without compost) is likely due the lower pH in those samples which promote the extraction of metals though protonation. Addition of compost decreased the mobility of the heavy metals as an organic amendment remediation.

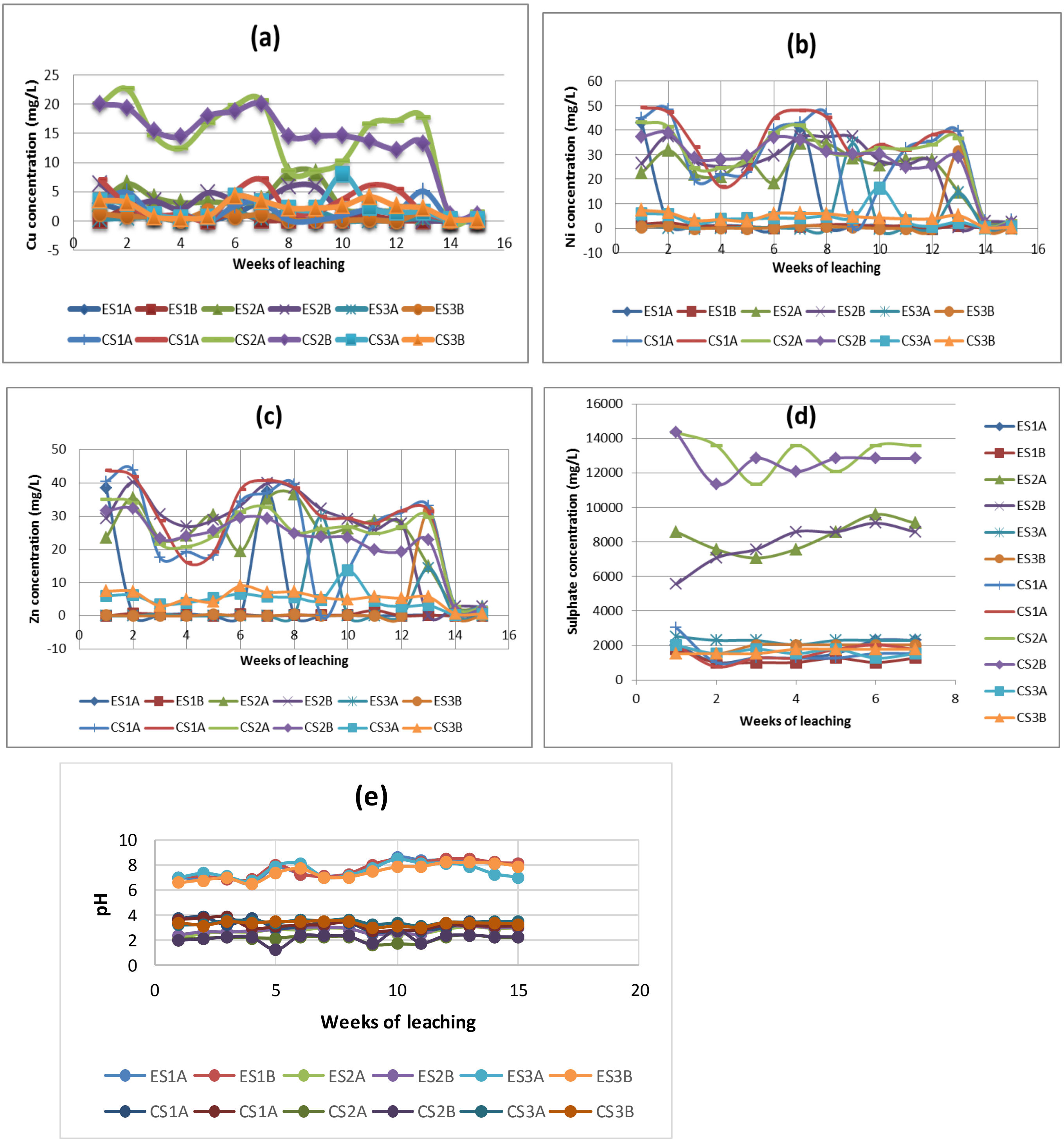

Figure 3: Column leaching results for the metals released (Cu, Ni and Zn), pH measured and sulphate concentration of leachates of mine tailings over 15 leaching weeks.

5.3.5. Major pollutants in the mine tailings

EC, Cl^-, SO_4^{-2}, pH and alkalinity levels at the end of the experiments (after 15 weeks) are shown in Table 3. The addition of compost increased the pH of the leachate, except in samples from the middle of the tailings dumps, which revealed the low pH values of 2.79 for ES2A and 2.02 for ES2B after treatment. The samples with pH higher than 7 had positive alkalinity values. Generally the leachate from the mine where acid mine drainage take place, show low pH values ranging between 2 and 4 (Jambor *et al.*, 2003; Alvarez, *et al.*, 2006; Bempah *et al.*, 2013). The SO_4^{-2} concentrations decreased when samples from S2 were treated with compost, some recorded values were 9090mg/L from ES2A and 8585 mg/L from ES2B, with the treated ones having high concentrations of 13590 mg/L and 12835 mg/L respectively. The samples from the top, (S1) and (S3) showed increased sulphate concentrations (2295 mg/L from ES3A, 2090mg/L from ES3B and 2 295 mg/L from ES1A) when they were treated. An exception was ES1B, from which rather lower concentration (1275 mg/L) was obtained. The high concentration of sulphate shows that the oxidation of sulphide minerals took place in the mine tailings (Bempah *et al.*, 2013). Addition of compost to the mine tailings sample decreased the chloride ion concentration. It was found in previous studies that addition of organic amendment to mine tailings increases the EC (Lam*et al.*, 2016). The redox potential for treated samples was found to decrease in this study, except in the leachate from ES2A where the redox potential value seems to have increased. The electric conductivity tested in the leachates ofuntreated samples of S1and S3 was higher than the composted samples (3.03 mS/cm and3.70 mS/cm for ES1A and ES1B, respectively, and 3.79 and 3.61mS/cm for ES3A and ES3B, respectively).No major difference was observed among the EC values of untreated and composted samples of S2, this is consequent to the lack of pH change observed above.

Table 4: measured values of major pollutants in the mine tailings

Sample ID	**Measured values of major pollutants in the tailings samples**					
	Primary Parameters			**Major anions**		
	pH	**Eh (mV)**	**EC (ms/cm)**	**SO_4^{2-} (mg/L)**	**Cl- (mg/L)**	**Alkalinity (mg/L)**
ES1-A	8.16	2.78	3.03	2295.00	433.33	12.50
ES1-B	8.13	2.82	1.70	1275.00	800.00	12.00
ES2-A	2.99	9.47	6.13	9090.00	1200.00	0.00
ES2-B	3.02	7.74	6.40	8585.00	1633.33	0.00
ES3-A	7.03	3.28	3.79	2295.00	2000.00	8.00
ES3-B	7.92	3.02	3.61	2040.00	2433.33	12.00
CS1-A	3.17	7.60	1.94	1530.00	2600.00	0.00
CS1-B	3.16	7.60	1.28	1785.00	2766.67	0.00
CS2-A	2.22	8.51	7.71	13590.00	3033.33	0.00
CS2-B	2.28	8.46	6.82	12835.00	3300.00	0.00
CS3-A	3.48	7.31	1.65	1530.00	3500.00	0.00
CS3-B	3.33	7.45	2.74	1785.00	3666.67	0.00

5.3.6 Metal speciation in the leachates of mine tailings

The speciation of metals in the leachates of mine tailings was predicted by using PHREEQC modelling software, which is built in an interface to the AQUACHEM application. The results of the speciation form of Cu, Ni and Zn have been reported as a percent range in Table 4**.** The model reports the speciation of metals in terms of free hydrated ion and complexed ions (Fosso-Kankeu *et al.*, 2016; Obiefuna and Orazulike, 2010). When using this model a variety of reactions may occur which promote the speciation and mobility of metal contaminants, which include acid/base, precipitation/dissolution, sorption and ion exchange reactions that can delay the movement of metals (Obiefuna and Orazulike, 2010). The most abundant species of Cu occurred as a complex with the hydroxide. Some studies have indicated that when metals form inorganic complexes, their availability as free hydrated is restricted, which decreases the mobility and bioavailability of metals to the hydrological system, which subsequently decreases the toxicity of metal (Korfali and Davis, 2004; Fosso-Kankeu *et al.*, 2016). One of the dominant speciation form of Cu, was found in the high percentage range, as free hydrated form (Cu^{+2}) and complexed with SO_4^{-2}. Ni was most abundant as a free hydrated species (with a percentage range of 0-65.92%) and when complexed with SO_4^{-2}. Other species of Ni predicted were $NiCl^+$ and $NiOH^+$ which had relatively low percentage ranges of 0-6.32%and less than 1%, respectively. The dominant species of Zn was the free hydrated ion form and the form complexed with SO_4^{-2}. Other species for Zn found had an oxidation state of +2. When a metal is found in high percentage as complexed form, it indicates that most of this metal will be available, but will cause less toxicity than the free hydrated metal ion, which is likely to contaminate the environment. In that regard Cu will be the most available metal in the tailings, as it has the highest percentage (96.67%) of free form, but complexation also partly limits its toxicity. Ni and Zn being also abundant as free ions, will be bioavailable and contribute to the increase of water toxicity.

Table 5:Percent range of dominant species distribution in a leachate of mine tailings

Element	Species	% Range
Cu	$Cu(OH)_2$	0-96.67
	Cu^{+2}	0-68.88
	$CuSO_4$	0-49.93
	$CuOH^+$	<1
Ni	Ni^{+2}	0-65.92
	$NiSO_4$	0-59.76
	$NiCl^+$	0-6.32
	$NiOH^+$	<1
Zn	Zn^{+2}	0-58.83
	$ZnSO_4$	0-44.77
	$ZnCl^+$	0-16.64
	$Zn(SO4)_2^{-2}$	0-4.87
	$Zn(OH)_2$	0-4.12
	$ZnOH^+$	0-2.50
	ZnOHCl	0-2.70

5.4. Conclusion

The present study investigated the effectiveness of the compost in mine tailings management. The results indicated that the addition of the compost decreased the mobility of metals (Cu, Zn and Ni). The addition of the compost did not have a major effect on the samples collected at the middle of the tailings dump as it had a lower pH, even after the treatment. Alkalinity was found only for samples from the top and the bottom of the tailings dump, as those samples had pHs ranging from 7 to above 8. When the compost was not applied to mine tailings which were characterized by low pH, elevated levels of toxic metals in the bioavailable form were mobilized; implying that these tailings could be dangerous to the ecosystem if not properly managed. The speciation of metals determined by using PHREEQC showed that Ni and Zn partly occurred as free ions, indicating that they can disperse in surface water and cause toxicity. CuOH was the overall predicted dominant species, but less toxic to the environment due to complexation with hydroxide ion. Sulphate was found in high concentrations in the tailings, mostly in the middle of the tailings dump, which indicates that the oxidation of sulphide has occurred and that it is able to cause AMD. Although further research is needed, compost appears promising as a good cover for mine tailings.

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References

Bempah **C.**K, Ewusi A, Obiri-Yeboah S, Asabere S.B, Mensah F, Boateng J, Voigt H, 2013. Distribution of Arsenic and Heavy Metals from Mine Tailings dams at Obuasi Municipality of Ghana. *American Journal of Engineering Research (AJER)*. 02(05), -61-70.

Brown S, DeVolder P, Compton H, Henry C, 2007. Effect of amendment C: N ratio on plant richness, cover and metal content for acidic Pb and Zn mine tailings in Leadville, Colorado. *Environmental Pollution*, 149, 165-172.

Du Toit S, 2011. Hidden Footprint of Gold Mining Activities in the West Rand: Some present and future concerns to be addressed. A Case Study.

Fosso-KankeuE, Manyatshe A, Waanders F, 2016.Mobility potential of metals in acid mine drainage occurring in theHighveld area of Mpumalanga Province in South Africa: Implication ofsediments and efflorescent crusts. International *Biodeterioration & Biodegradation*. 1-10

Flores A.N, Sola F.M, 2010. Evaluation of Metal Attenuation from Mine Tailings in SE Spain (Sierra Almagrera): A Soil-Leaching Column Study. *Mine Water Environ*. 29, 53–67

Forsberg L.S, J Gustafsson & D.B Kleja & Ledin S, 2008. Leaching of Metals from Oxidising Sulphide Mine Tailings with and without Sewage Sludge Application. *Water Air Soil Pollut*.194:331–341

Grover B.P.C, Johnson R.H and Tutu H, 2016. Leachability of metals from gold tailings by rainwater: an experimental and geochemical modelling approach. *Water SA*. 42-1

Jia y, Maurice C, Ohlander B, 2014. Metal Mobilization in Tailings Covered with Alkaline Residue Products: Results from a Leaching Test Using Fly Ash, Green Liquor Dregs, and Lime Mud. *Mine Water Environ*.

Kaartinen T & Wahlstrom M, 2009. Development of a European standard for the determination of acid potential and neutralization potential of sulfidic waste - 8th *International Conference on Acid Rock drainage*.

Kim H.J, Kim Y, Choo C.O, 2014.The effect of mineralogy on the mobility of heavy metals in mine tailings: a case study in the Samsanjeil mine, Korea. *Environ Earth Sci*. 71, 3429–3441

Kundu S, Rathore A.S, Pushp A & Chundawat V.S, 2014. Batch investigations on elemental dissolution from copper mine tailings pond, Khetri, India: Evaluation of the environmental. contamination potential international conference on *Chemical, Civil and Environmental Engineering* (CCEE'2014). 18-19.

Lackovic A.J.A, Nikolaidis N.P, Chheda P, Carley R.J and Elsie P, 2007. Evaluation of bath leaching procedures for estimating metal mobility in glaciated soil. *Ground water & Remediation*. 17, 231-240.

Lam E.J &. Gálvez M. E & M. Cánovas2 & I. L. Montofré1 & D. Rivero1 & A. Faz3, 2016. Evaluation of metal mobility from copper mine tailings in northern Chile. *Environ Sci Pollut Res*. 11356-016-6405

Lawrence R.W & Scheske M, 1997. A method to calculate the neutralization potential of mining wastes. *Environmental Geology*. 32 (2).

Liefferink, 2011.Assessing the past and the present role of the National Nuclear Regulator as a public protector against potential health injuries: *The West and Far West Rand as case study*.

Malatse M & Ndlovu S, 2015.The viability of using the Witwatersrand gold mine tailings for brickmaking. *Southern African Institute of Mining and Metallurgy*. 115, 321-327.

Novhe N.O., Yibas B., Netshitungulwana R. and Lusunzi R. 2014. Geochemical and minerological characterization of mine residue deposits in the Komati/Crocodile catchment, South Africa: an assessment for acid/alkaline mine drainage *ISBN*. 978-7-5646-2437-8.

Oelofse S.H.H, Hobbs P.J, Rascher J & Cobbing J.E, 2007. The pollution and destruction threat of gold mining waste on the Witwatersrand - *A West Rand case study*.

CHAPTER 6

Conclusions and Recommendations

6.1 Conclusions

This study has satisfied the aim and objectives that were set in Chapter 1, so in this section the concluding remarks are made, based on the objectives set.

This work presents the findings of the investigation of the metal mobility from the mine tailings dumps under the influence of the following: environmental conditions, organic acids, and microorganisms. The results indicated that the top of the tailings dump consisted mostly of oxide minerals, while the bottom of the dump contained sulphide minerals. The mineralogical structure had an influence in the mobility of metals, as it was found that the metals at the top layer of the dump had higher mobility than that from the bottom when sequential leaching was conducted. That might be due to the fact that oxidation at the top of the tailings dump was more extensive than at the bottom. The results from sequential leaching test further showed that most metals were less mobile from the residual fractions than in the most labile fractions. Therefore, metals were released from the labile fractions than from the residual fraction where metals were bound to organic matter. The heterotrophic and autotrophic microorganisms identified in the tailings have the potential to mobilize metals through acidolysis and complexolysis. Groups identified by using FTIR analysis are likely to bind metals and prevent their mobility.

The autotrotrophic microorganisms found were *Leptospirillum* sp and *Sulfobacillus* sp, whereas the heterotrophic microorganisms were *Bacillus* sp and *Pseudomonas* sp.The batch leaching results with the use of organic acids showed that Al and Fe mobility was influenced by environmental conditions. Citric and oxalic acids were found to be the most efficient leaching agents. Al and Fe had high mobility in acidic media and at high temperatures. When organic acids acted together (synergy) they were more efficient than when acting individually. This could be ascribed to the diversity of leaching mechanisms. Kinetic studies were used to determine the rate limiting steps for the dissolution of metals, which was essential for the improvement of leaching rate. It was shown that the reaction rates were controlled by diffusion and the leaching rate was therefore influenced by the physical properties of tailings. The simulation of fieldrealities were assessed by the use of column leaching experiments with fresh tailings samples from a tailings dump. Compost as an organic amendment was combined with tailings in column experiments. The results indicated that Cu, Ni and Zn mobility decreased when tailings from the top and bottom of the tailings dump were combined with compost. The addition of compost did not have an effect on sample from the middle of the tailings dump, as it remained acidic. The PHREEQC model results showed that the occurrence of the Ni and Zn as free metal ions will enhance their mobility in the surface and will contribute to pronounced pollution. Sulphate was abundant in the tailings leachates, which indicated the presence of sulphide likely to contribute to the formation of AMD.

6.2 Recommendations

The following recommendations for further studies are made, based on the results found.

For a column leaching experiment, the rainwater must be used as leaching agent in order to simulate the field situation exactly.

Other organic amendments should be used for the middle of the tailings dump samples, as compost did not show any effect on the mobility of metals.

For batch leaching experiments inorganic acids should be used to leach out metals from the same area in order to compare the results with those found in the current study in which organic acids were used.

Appendix A

Calculation Formulas

Organic carbon

Organic carbon (%) = 0.003 g × N × 10 Ml × (1-T/S) × 100 / ODW

= 3 (1 – T/S) / W

Where: N = Normality of $K_2Cr_2O_7$ solution

T= volume of $FeSO_4$ used in sample titration

S= volume of $FeSO_4$ used in blank titration

ODW = Oven-dry sample weight (g)

The Neutral Potential:

Modified NP (kg $CaCO_3$/t) = [(N x vol (ml) of HCl) – (N x vol (ml) NaOH) x 50] / [weight of sample (g)]

Total Alkalinity

Total alkalinity = (Volume of H_2SO_4 ×1000)/ (Volume of sample)

Total Chloride

Total chloride = $(V_1 \times 1000) / (\text{sample volume})$

Where V_1 = volume of titration

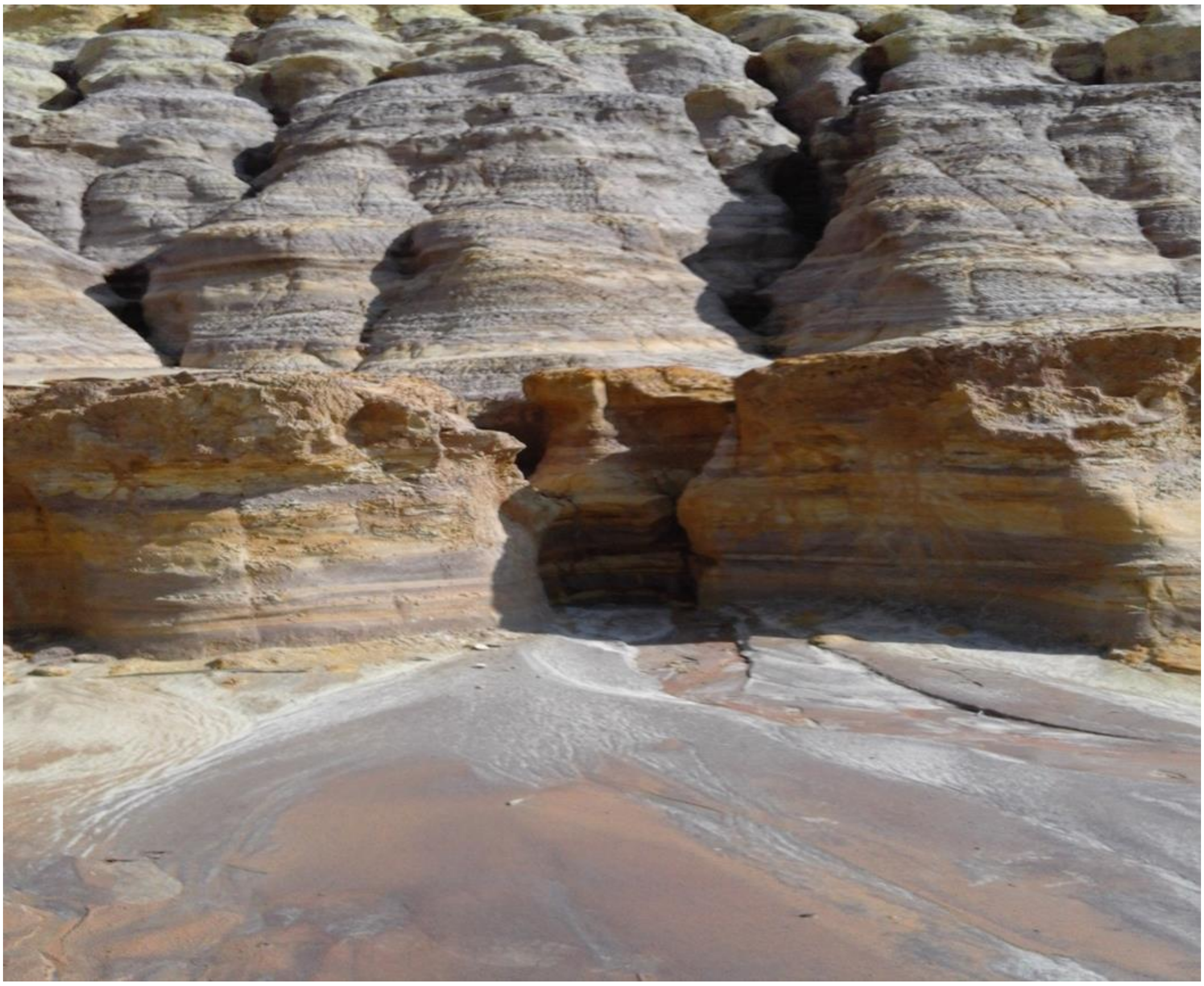
Appendix B

Sampling site pictures

Picture 1: Sampling from the top of tailings dump- flat surface 1

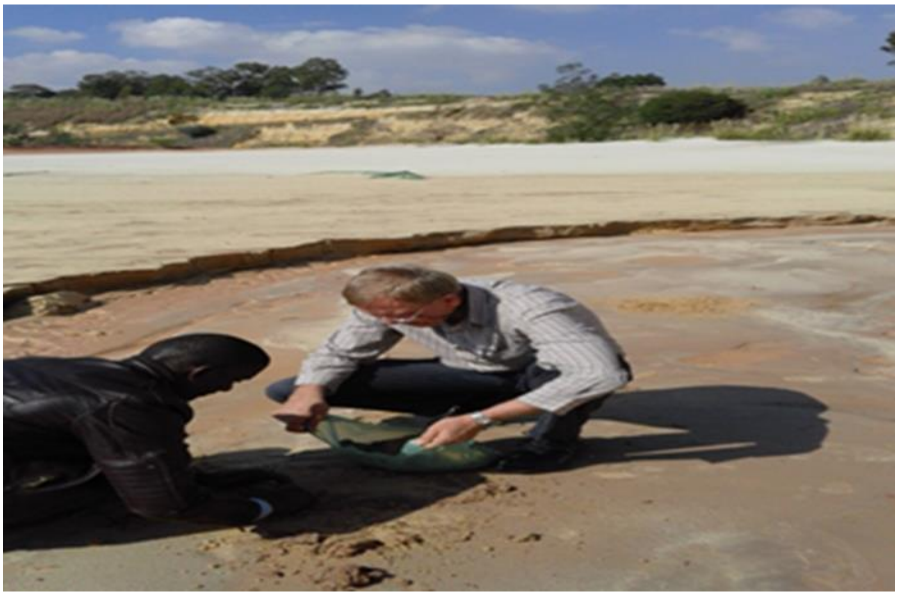
Picture 2: Sampling from the top of the tailings dump- flat surface 2

Picture 3: Middle of the tailings dump



Picture 4: Eroded tailings from the middle of the dump

Picture 5: Bottom of the tailings dump and its wash away from the top of the dump



Picture 6: Sampling from the bottom of tailings dump

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Mobility of Metals from Mine Tailings using Different Types of Organic Acids: Batch Leaching Experiment

Ashley H. Munyai[1], Elvis Fosso-Kankeu[2], Frans Waanders[3]

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Abstract: ***The presence of toxic metals in mine tailings is a major concern because they are hazardous to ecological system and human health. Hence the mobility of heavy metals is an important factor to look at when assessing risk of pollution or contamination in tailing dump. This study was carried out in order to determine the effect of organic acids on the mobility of metals from mine tailings. Characterization of mine tailings was carried out using XRD and XRF. Batch leaching experiment under different initial pH, contact time, temperature, and concentration was carried out in this study. The results show that Fe and Al were the major elements, whereas quartz minerals were considered as the major constituents in the tailing. The batch leaching studies indicated high mobility of elements at low pH, short exposure time, high concentration of organic acids and high temperature. Increase of temperature resulted to faster release of metals, with maximum concentrations of Fe and Al recorded at 48 hours. Oxalic acid and citric acid were found as best leaching agents. The kinetic studies allowed to predict that the dissolution of metals from tailing samples was mostly diffusion controlled.***

Keywords: Mine tailings, batch leaching, organic acids, mobility of metals, pH, temperature, concentration

1. Introduction

The exploitation of mineral resources provides strategic resources, but heavy metals contaminations in the soil and water has become one of the environmental problem within the vicinity of mines (Ding et al., 2014; Conesa and Schuling, 2010). Mining operations introduce various heavy metals into the soil and water. As chemical hazards heavy metals are non biogradable and can remain in the environment for a long period of time (Wuana et al., 2010). These metals are released from mine wastes. South Africa produce an estimated 468 million tons of mineral wastes (Oelefse et al., 2007), and most of it is produced by gold mines accountingfor221 million tons or 47% of all mineral wastes produced, making it the largest source of pollution. Among all the wastes, mine tailings are known to be the main environmental effect (Conesa et al., 2007; Dudka and Adriano, 1997) because of its low pHs (Wong et al., 1998; Conesa et al., 2007).

Decontamination of the mine tailings is required to protect the environment (Seh-Bardan et al., 2012). The conventional methods such as soil, venting incineration, physical treatment and chemical treatment are being used for the removal of metals from contaminated soil (Praburaman et al., 2015). This convectional mineral process recently used to recover metals, but these metals have disadvantages such as high costs, long repair cycle and low efficiency (Zhong-bing et al., 2011; Dong et al., 2011). In comparison to the conventional methods, bioleaching is more effective to treat low-low grade tailings because many advantages such as low cost, low investment fast processing, simple equipment, wide range of applications, easy management and environment friendliness (Dong etal.,2011). Bioleachingis basically "the use of microorganisms to transform elements so that the elements can be extracted from a material when water is filtered through it" (Brandl, 2001; Mishra et al., 2005;Brandl and Faramarzi, 2006).Microorganisms can mobilize metals trough autotrophic and heterotrophic metabolites and siderophores and methylation which can result in volatilization (Mishra and Rhee, 2014). Microbes action on metals is based on three principles namely acidolysis, complexolysis and redoxolysis (Brandl and faramarzi, 2006). In these processes/ mechanisms microorganisms are able to mobilize metals by the formation of organic or inorganic acids (e.g. citric, oxalic acids and sulfuric acid (acidolysis). In the case of complexolysis processes, the metal solubilization is by ligand-induced mechanisms where microbial formation of complexing or chelating agents increases the metals mobility (Mishra and Rhee, 2014).

Organic acids can supply both protons and metal complexing anions (Gadd, 2004). Citrate form stable complexes with a number of metal ions, for example copper, zinc and highly mobile complexes may be resistant to biodegradation (Gadd, 2001). The reason why this low molecular weight (LMW) anion works as organic ligand, is because of its ability to promote the mobility of heavy metals from contaminated soil by (i) replacing adsorbed metals at the soil surface through ligand-exchange reactions, (ii) dissolving metal-oxides from surfaces that have adsorbed metals, and (iii) forming metal-organic complexes in solution (McColl and Pohlman, 1986; Pohlman, 1986; Stone, 1988; Banks et al 1994; Burckhard et al., 1995; Kim et al., 2013). Such anions increase the mobilization of metals from soil. Most studies have focused on the effect of organic acids on the mobility of metals from soils and sediments, however there is less information regarding their release from mine tailings and there is a need to confirm such findings in South Africa as this type of studies have been done in other countries. In this study batch leaching process was applied using organic acids in order to assess the mobilization of metals from mine tailings. Hence the objective of this study is to determine the effects of contact

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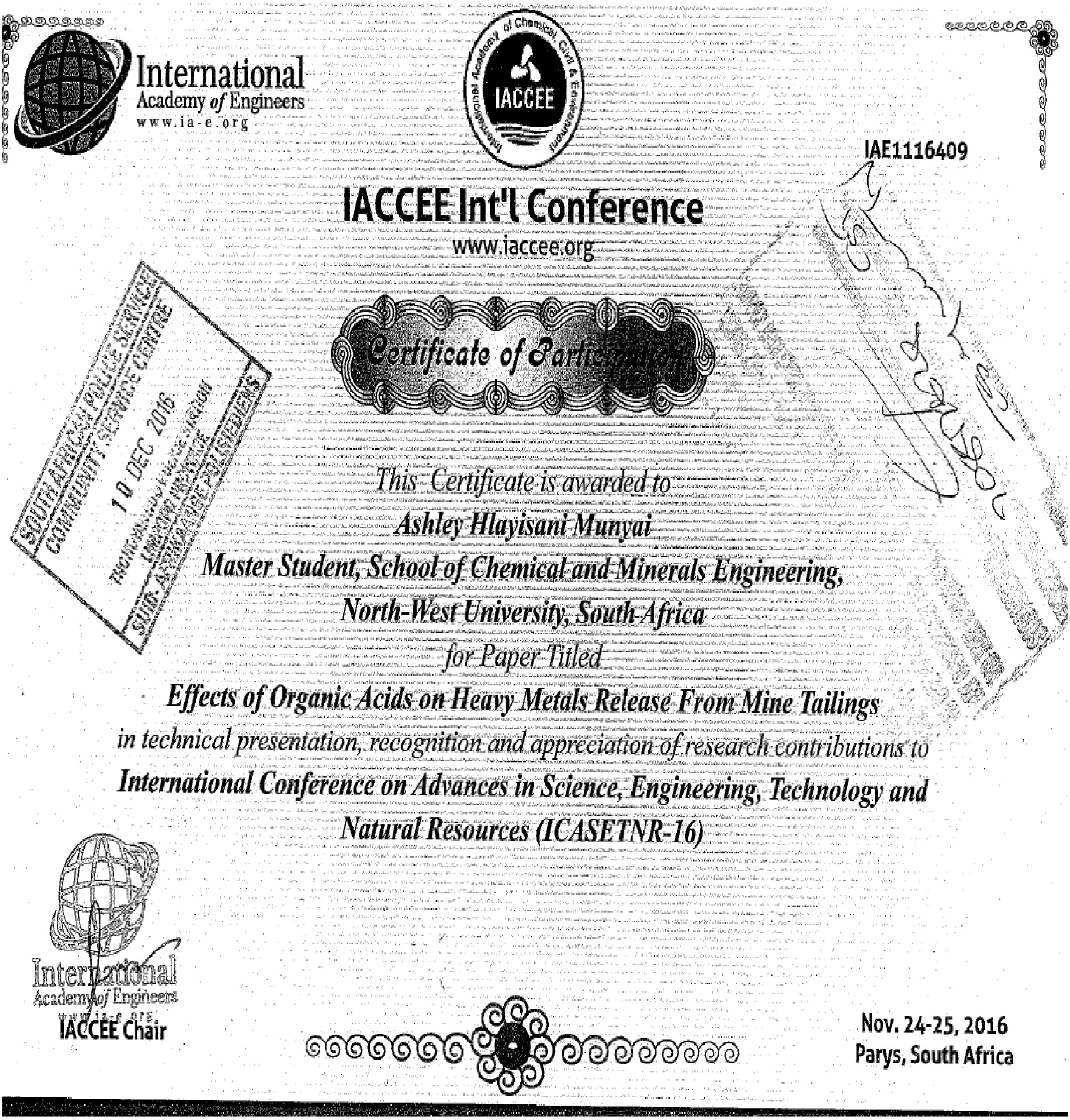

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